ineering
Library

JUL 22 '46

UNITED STATES DEPARTMENT OF COMMERCE

Journal of Research

of the

National Bureau of Standards

Vol. 36, No. 5 May 1946

CONTENTS

RP	TITLE AND AUTHOR	Page
1712.	An analysis of the effects of fuel distribution on engine performance. Donald B. Brooks.....[Price .05 cents]	425
1713.	Effects of mildew on vegetable-tanned strap leather. Joseph R. Kanagy, Arbelia M. Charles, Edward Abrams, and Rees F. Tener.....[Price .05 cents]	441
1714.	Heats of combustion and formation at 25° C of the alkylbenzenes through $C_{10}H_{14}$ and of the higher normal monoalkylbenzenes. Edward J. Prosen, Walter H. Johnson, and Frederick D. Rossini..[Price .05 cents]	455
1715.	Heats of combustion of four cyclopentane and five cyclohexane hydrocarbons. Walter H. Johnson, Edward J. Prosen, and Frederick D. Rossini.....[Price .05 cents]	463
1716.	Size grading of diamond powders. B. L. Steierman, H. Insley, and W. H. Parsons.....[Price .05 cents]	469
1717.	Precision of telescope pointing for outdoor targets. Francis E. Washer and Helen Brubaker Williams.....[Price .05 cents]	479

The articles listed may be purchased separately (see cover page II) at the prices stated

A monthly periodical of pure and applied science published by our national Government

Journal of Research
of the
National Bureau of Standards

The January 1946 issue of the JOURNAL OF RESEARCH of the National Bureau of Standards began the thirty-sixth semiannual volume of this periodical. Fundamental researches in progress in the Bureau's laboratories are reported in this JOURNAL. If you are interested in new developments in science and technology, you should receive the JOURNAL. If you are not already a subscriber, you are invited to send in your subscription.

Technical News Bulletin

This is a monthly publication containing short articles reporting progress of work in the Bureau laboratories, abstracts of papers that appear in the JOURNAL OF RESEARCH, accounts of scientific and technical meetings in which the Bureau has taken part, a list of all publications by members of the staff, and other items within the Bureau's fields. The BULLETIN is designed primarily to give a general and timely review of the activities of the Bureau in brief form. It is a prompt and reliable source of official information. If you have not already subscribed for the BULLETIN, you are invited to do so.

ANNUAL SUBSCRIPTION	Price	
	United States, Canada, Cuba, Mexico, Newfoundland, Republic of Panama	Other countries
JOURNAL OF RESEARCH of the National Bureau of Standards:		
12 monthly issues (2 volumes), paper covers	$3.50	$4.50
Bound volume (½ year, 1 volume), blue buckram	3.00	3.50
Technical News Bulletin, 12 monthly issues	.50	.70

Research Papers, reprinted individual articles appearing in the JOURNAL OF RESEARCH, are available from the Superintendent of Documents shortly after appearance of monthly issues of the JOURNAL.

Address orders only to
Superintendent of Documents, U. S. Government Printing Office
Washington 25, D. C.

UNITED STATES DEPARTMENT OF COMMERCE
HENRY A. WALLACE, Secretary
NATIONAL BUREAU OF STANDARDS
E. U. Condon, Director

✦

Journal of Research

of the

National Bureau of Standards

✦

Volume 36, Number 5

May 1946

[Published with approval of the Director of the Budget]

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1946

For sale by the Superintendent of Documents, U. S. Government Printing Office
Washington 25, D. C. - Price 30 cents, $3.50 per year on subscription

The prices of the separate Research Papers appearing in this JOURNAL are given on the front cover page. If 100 or more copies of any separate are ordered, a discount of 25 percent is allowed. Those who desire copies of separate Research Papers should send their orders and remittances without delay to the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. Research Papers are not printed from electrotypes, and usually no more reprints can be had when the first and only printing is exhausted.

MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on pages 3 and 4 of the JOURNAL cover. New tables will be announced from time to time as they become available. An order blank is available on the last page of this issue.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1712

Part of Journal of Research of the National Bureau of Standards, Volume 36, May 1946

AN ANALYSIS OF THE EFFECTS OF FUEL DISTRIBUTION ON ENGINE PERFORMANCE

By Donald B. Brooks

ABSTRACT

From an empirical equation, based on single-cylinder-engine test data and relating engine power to fuel consumption, engine-performance curves are derived analytically for typical examples of poor mixture distribution. Investigation of the resulting information shows that the minimum specific fuel consumption is a satisfactory criterion of distribution quality. A method is developed for ascertaining the attainable improvement over a given distribution.

CONTENTS

		Page
I.	Objective of analysis	425
II.	Derivation of formulas	426
III.	Study of different types of maldistribution	428
IV.	Study of different degrees of maldistribution	433
V.	Estimation of improvement attainable	436
VI.	Factors not considered in analysis	438
VII.	Conclusions	439
VIII.	References	439

I. OBJECTIVE OF ANALYSIS

The effects of imperfect fuel distribution on engine performance were well known to automotive engineers a generation ago, when the increasing demand for gasoline was overtaxing the simpler refining processes then available and making it necessary to include components of relatively low volatility in motor fuel. With the advent of cracking processes, gasoline has since become a more satisfactory fuel, and manifolding an engine is no longer as much of a problem as it was. Recent work [1, 2] [1] at this Bureau on substitute motor fuels, carried on at the request of and sponsored by the Foreign Economic Administration, showed that certain substitute fuels were distributed very poorly in manifolds designed for use with gasoline. With 190-proof alcohol, for example, distribution was so bad that it would seem economical to redesign the manifold for use with alcohol, if any considerable number of engines of one type were to be operated on this fuel regularly.

As such a redesign would probably involve some compromise, because of the variable composition of substitute fuels, it seemed desirable to reexamine the effect of fuel distribution on performance. Sparrow, in "The Arithmetic of Distribution" [3], presented a graphical

[1] Figures in brackets refer to literature references at the end of this paper.

analysis of specific manifold deficiencies on power and specific fuel consumption. In the present work, an analytical method has been used, as it is more flexible and better adapted for determining certain other relations, such as the fuel-flow rates at which minimum specific fuel consumption and maximum power occur.

II. DERIVATION OF FORMULAS

The computations of this analysis are based on data obtained in single-cylinder-engine tests of various fuels [1], involving some 800 measurements of engine power. These data are shown in figure 1. A smooth curve was faired through these data, plotted as percentage of maximum power against percentage of fuel consumption at peak power. Tangents to this curve were obtained graphically, and were plotted, figure 2. A formula was then sought to fit the data shown in figure 2. This method of obtaining a formula fitting the derivative, then integrating to get the desired function, has often been found more successful than the direct approach.

After several attempts, the data were fitted, as shown by the solid curve in figure 2, by the formula

$$\frac{dy}{dx}=\frac{132300}{x^3}-\frac{3186.9}{x}+25.651-0.07012x, \tag{1}$$

where

y=power, percentage of maximum

x=fuel consumption, percentage of that at maximum power.

Upon integration and substitution of the peak coordinates to evaluate the constant of integration, this becomes

$$y=-\frac{132300}{x}-7338.108 \log x+13884.716+25.651x-0.03506x^2. \tag{2}$$

This equation, which is plotted in figure 1, gives the relation of power to fuel consumption for the single-cylinder engine, and by extension, for a similar multicylinder engine having perfect distribution at all mixture ratios.

In applying eq 2 to cases of multicylinder engines with imperfect distribution, x and y have the significances indicated above, with the addendum "for perfect distribution" to the definition of each. In addition, X, with an appropriate subscript, is defined as the ratio of the fuel delivered to a given cylinder to the average fuel delivered per cylinder. The equation for an engine of "n" cylinders, having the distribution represented by X_1, X_2, . . . X_n is then obtained by replacing the "x" of eq 2 with

$$x\frac{\Sigma_1^n f(X)}{n},$$

where $f(X)$ is of the same degree in X as the term in eq 2 for which it is being substituted is in x. Thus in the first term of eq 2, x is replaced by

$$x\frac{\Sigma_1^n \left(\frac{1}{X}\right)}{n}.$$

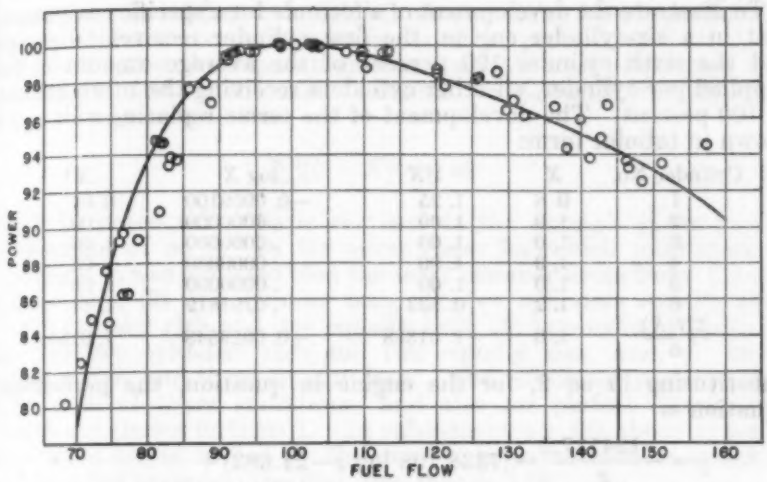

FIGURE 1.—*Single-cylinder-engine test data on which analysis was based.*

The curve represents the equation that was fitted to these data. Coordinates were chosen so that a maximum power of 100 was reached at a fuel flow of 100.

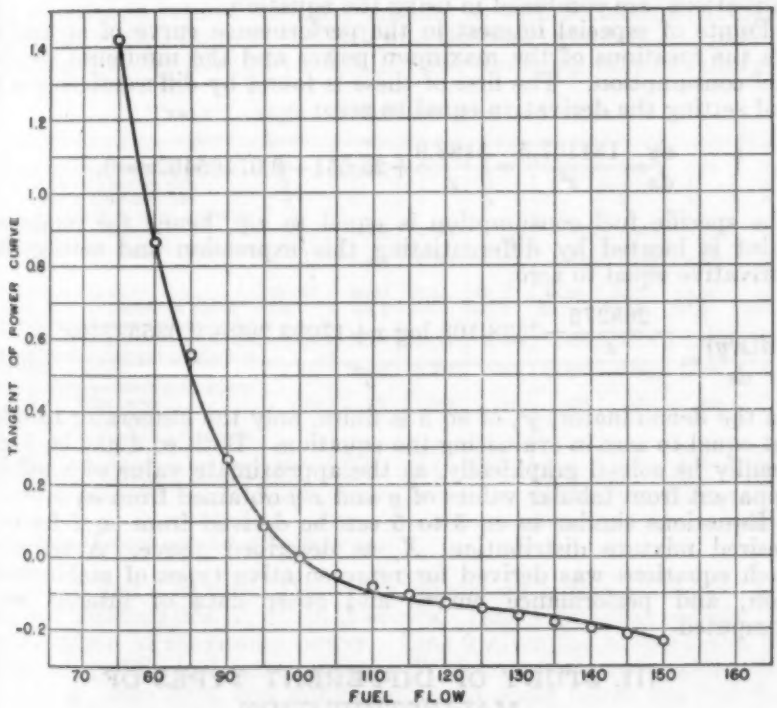

FIGURE 2.—*Tangents of power curve shown in figure 1.*

The circles show the tangent values derived graphically from the data of figure 1; the curve represents the equation which was fitted to these tangents.

To illustrate the development of a formula for a specific case, assume that in a six-cylinder engine, the first cylinder receives 80 percent and the sixth cylinder 120 percent of the average amount of fuel supplied per cylinder, all other cylinders receiving the mean amount, or 100 percent. The development of the terms replacing x in eq 2 is shown in tabular form:

Cylinder No.	X	$1/X$	$\log X$	X^2
1	0.8	1.25	−0.0969100	0.64
2	1.0	1.00	.0000000	1.00
3	1.0	1.00	.0000000	1.00
4	1.0	1.00	.0000000	1.00
5	1.0	1.00	.0000000	1.00
6	1.2	0.833	.0791812	1.44
$\frac{\Sigma_1^6 f(X)}{6}$	1.0	1.01388	−0.0029548	1.0133

Substituting in eq 2, for the engine in question, the performance equation is

$$y=-\frac{134137.5}{x}-(7338.108\log x-21.683)+$$
$$13884.716+25.651x-0.03552746x^2 \quad (3)$$

The two constant terms, shown separately in eq 3 to indicate their derivations, are combined in using the equation.

Points of especial interest in the performance curve of an engine are the locations of the maximum power and the minimum specific fuel consumption. The first of these is found by differentiating eq 3 and setting the derivative equal to zero:

$$\frac{dy}{dx}=\frac{134137.5}{x^2}-\frac{3186.9}{x}+25.651-0.07105492x=0. \quad (4)$$

The specific fuel consumption is equal to x/y, hence the minimum point is located by differentiating this expression and setting the derivative equal to zero:

$$\frac{d(x/y)}{dx}=\frac{-\frac{268275}{x}-7338.108\log x+17093.299+0.03552746x^2}{y^2}=0. \quad (5)$$

As the denominator, y^2, of eq 5 is finite, only the numerator need be set equal to zero in evaluating the equation. Both eq 4 and eq 5 can readily be solved graphically, as the approximate value of x will be apparent from tabular values of y and x/y obtained from eq 3.

Equations similar to eq 3 to 5 can be derived from eq 2 for any desired mixture distribution, X, as described above. A series of such equations was derived for representative types of maldistribution, and performance curves and other data of interest were computed.

III. STUDY OF DIFFERENT TYPES OF MALDISTRIBUTION

All computations were based on use of a six-cylinder engine. Computations for an eight-cylinder engine would be more lengthy, with

little increase in information yielded, whereas those for a four-cylinder engine would not give as many aspects of the problem as desired.

The first series of computations was made for a set of assumed distributions all having the same variance. Specifically, the distributions were so arranged that

$$\sum_1^6 (1-X)^2 = 0.08. \tag{6}$$

It will be noted that this is the case in the example given in the development of eq 3. In the seven cases for which computations were made, it was assumed that the total variance arose from: (1) one cylinder rich, (2) one cylinder lean, (3) two cylinders equally rich, (4) one cylinder rich and one equally lean, (5) two cylinders equally lean, (6) two cylinders rich and two equally lean, and, (7) three cylinders rich and three equally lean. The calculated performances under each of these conditions, and also for perfect distribution (case 0) are shown in table 1. In subsequent use the above types of distribution are identified by the number in parenthesis to which is appended the variance; the first case thus is 1.08.

Lines 2 and 3 of table 1 list the number of cylinders receiving richer and leaner mixtures than would be the case if perfect distribution prevailed. The number of cylinders not covered in lines 2 and 3 are assumed to receive the same mixture as with perfect distribution. The relative fuel flows to the rich and the lean cylinders are given in lines 4 and 5, the flow for perfect distribution being taken as unity.

TABLE 1.—*Effect of distribution on performance*

1. Case number (variance of 0.08)	0	1.08	2.08	3.08	4.08	5.08	6.08	7.08
2. Number of cylinders rich	0	1	5	2	1	4	2	3
3. Number of cylinders lean	0	5	1	4	1	2	2	3
4. Relative fuel to each cylinder, rich		1.258	1.052	1.163	1.200	1.082	1.141	1.115
5. Relative fuel to each cylinder, lean		0.948	0.742	0.918	0.800	0.837	0.859	0.885
6. Maximum power	100.00	99.44	98.13	99.23	98.86	98.76	99.00	99.04
7. Fuel flow for maximum power	100.0	103.1	108.5	104.2	105.4	106.2	105.2	105.1
8. Specific fuel consumption at maximum power	1.000	1.037	1.105	1.050	1.066	1.075	1.062	1.061
9. Minimum of curve of specific fuel consumption*	0.851	0.879	(0.917)	0.886	(0.896)	(0.900)	(0.893)	0.892
10. Minimum specific fuel consumption in firing range	.851	.879	.978	.886	.923	.906	.895	.892
11. Fuel flow at minimum of specific fuel consumption curve	77.0	79.0	80.7	79.3	79.7	80.0	79.6	79.6
12. Firing range, minimum fuel flow	70.0	73.8	94.4	76.2	87.5	83.7	81.5	79.1
13. Firing range, maximum fuel flow	160.0	127.2	152.1	137.5	133.3	147.9	140.2	143.4
14. Firing-range ratio	2.29	1.72	1.61	1.80	1.52	1.77	1.72	1.81

*Parentheses indicate value lies outside firing range.

Lines 6 and 7 of table 1 give the maximum power developed, and the fuel consumption at which it occurs. Line 8 gives the specific fuel consumption at maximum power. Line 9 gives the minimum of the curve of specific fuel consumption. With some cases of maldistribution, e. g., case 2.08, this minimum would occur below the fuel flow at which all cylinders will fire. (The firing range is considered, from the single-cylinder-engine test data, to lie between fuel flows of 70 and 160, for perfect distribution). Line 10 gives the minimum specific fuel

consumption attained when the leanest cylinder is on the lean boundary of the firing range. Line 11 gives the fuel flow at the minimum of the curve of specific fuel consumption. The boundary fuel flows for regular firing are given in lines 12 and 13. In line 14 is given the ratio of fuel flow at the rich boundary to that at the lean boundary of the firing range. These boundaries are, of course, determined by the fuel flow to the engine when the leanest cylinder is receiving a relative fuel flow of 70 and when the richest receives 160.

It is apparent from table 1 that distributions having the same variance can differ greatly in their effect on performance. Thus the power

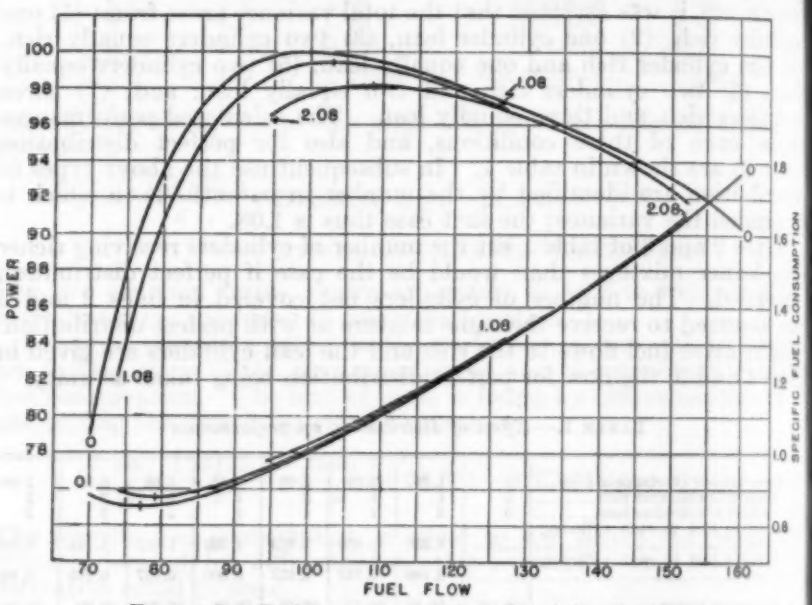

FIGURE 3.—*Performance curves for selected distributions.*

Case 0 is for perfect distribution, case 1.08 is for one cylinder rich, and case 2.08 is for one cylinder lean. The term .08 on the case number indicates the total variance of the distribution, defined by eq 6.

loss for case 2.08 is over three times that for case 1.08, and the deterioration of minimum specific fuel consumption is over four times as great as for case 1.08. The type of the distribution is of as much importance as the total variance. For a given variance, the worst type is that in which one cylinder is leaner than the remaining cylinders.

The power and the specific fuel consumption curves for cases 0, 1.08, and 2.08 are shown in figure 3. The loss of power is greater, and the increase in minimum fuel consumption is much greater in case 2.08 (one cylinder lean) than in case 1.08 (one cylinder rich), as compared with perfect distribution. The crosses in figure 3 mark the maxima of the power curves and the minima of the specific fuel consumption curves. As shown in figure 3, and also by line 8 of table 1, if the carburetor were set to give maximum power, the specific fuel consumption for case 2.08 would be more than 10 percent greater than with perfect distribution, whereas for case 1.08, it would be not quite 4 percent greater.

Cases 3.08 and 5.08 are similar to cases 1.08 and 2.08, respectively, but with much less departure from ideal performance. Case 4.08 (one cylinder rich, one lean) is intermediate between cases 1.08 and 2.08, whereas cases 6.08 and 7.08 are similar to case 4.08, but with less marked departures from the ideal.

In figure 3, all of the performance curves are plotted against the same fuel flow and power scales, these being chosen so that a maximum power of 100 is obtained with perfect distribution (case 0) at a fuel-flow rate of 100. On this figure, it is easy to recognize an improvement in distribution by the approach of the performance curves to those of the ideal case. In actual practice, however, the power and

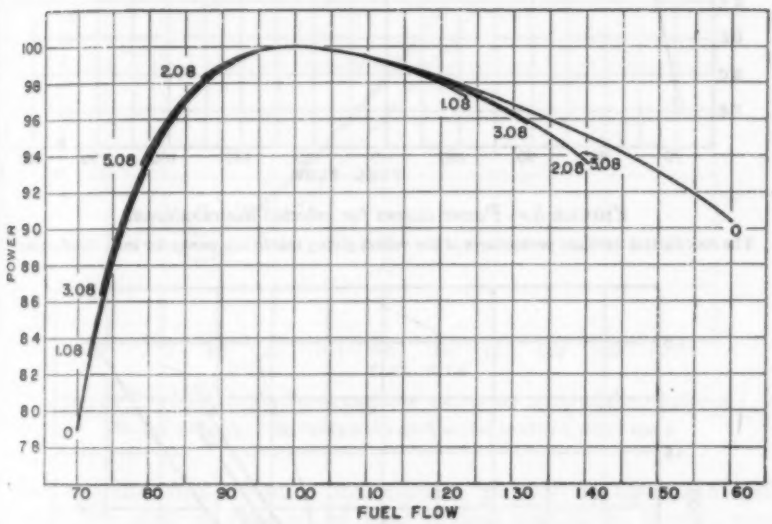

FIGURE 4.—*Power curves for selected distributions.*

The coordinates used are percentages of the values giving maximum power for each distribution.

fuel-flow rates for perfect distribution are not ordinarily known. Maximum power, and the rate of fuel flow at which it occurs, vary with atmospheric conditions [4, 5], and with other factors. Because of this, it is not determinable with sufficient accuracy to serve as a comparative basis for determining improvement in distribution. Furthermore, if the power curve for each distribution is plotted on scales such that its maximum power is 100 and occurs at a fuel-flow rate of 100, the curves for the different distributions having equal variance are nearly indistinguishable except for range, as can be seen in figures 4 and 5. The curves in figure 5 for cases 4.08, 6.08, and 7.08 are also practically identical with the curves for cases 1.08, 2.08 3.08, and 5.08 in figure 4. Thus changes in distribution are not accompanied by discernible changes in the shape of the power curve. In actual testing, the information obtained would suffice to plot curves such as figures 4 and 5, but not figure 3.

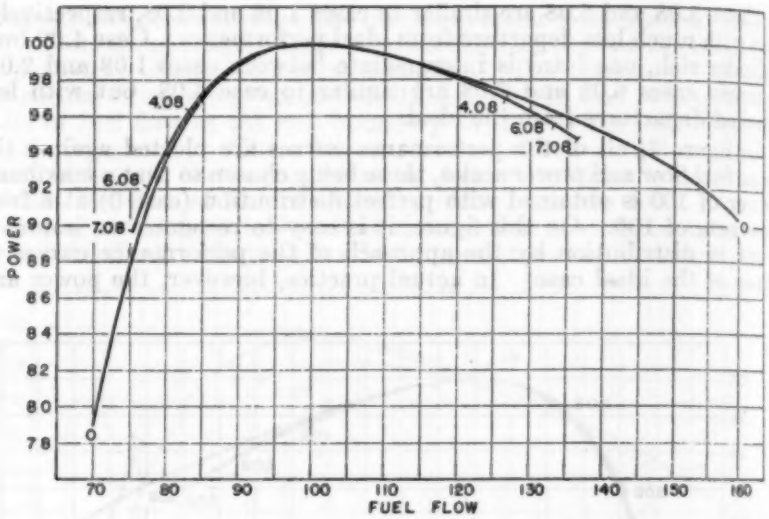

FIGURE 5.—*Power curves for selected distributions.*

The coordinates used are percentages of the values giving maximum power for each distribution.

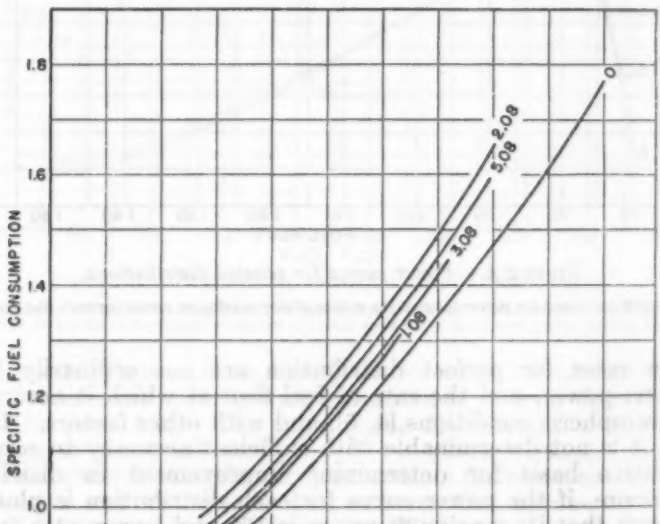

FIGURE 6.—*Specific fuel consumption curves for selected distributions.*

The abscissa scale of this figure is the same as that used in figures 4 and 5.

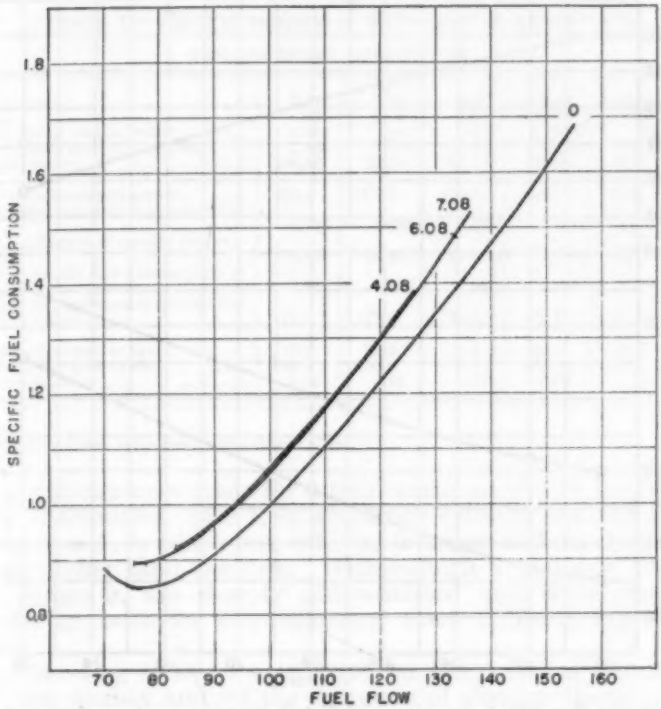

FIGURE 7.—*Specific fuel consumption curves for selected distributions.*
The abscissa scale of this figure is the same as that used in figures 4 and 5.

The specific fuel-consumption curves, plotted in figures 6 and 7 against fuel flow in percent of that giving maximum power, would appear to distinguish readily between good and bad distributions. To determine whether this is generally true, information on other distributions is required.

IV. STUDY OF DIFFERENT DEGREES OF MALDISTRIBUTION

For the maldistribution considered thus far, different types having equal variance have been studied. The poorest of these types, case 2, in which one cylinder was leaner than the rest, was chosen as the subject for a series of computations to determine the effect of variance of the distribution on performance factors. In addition to the variance of 0.08, used in case 2.08, values of 0.02, 0.04, 0.06, and 0.16 were used. The results of these computations are given in table 2. All performance factors of interest are seen to deteriorate at a somewhat accelerated rate with increase of variance. This is more readily noted from figure 8, in which maximum power, the specific fuel consumption at maximum power, and the minimum specific fuel consumption are plotted against variance.

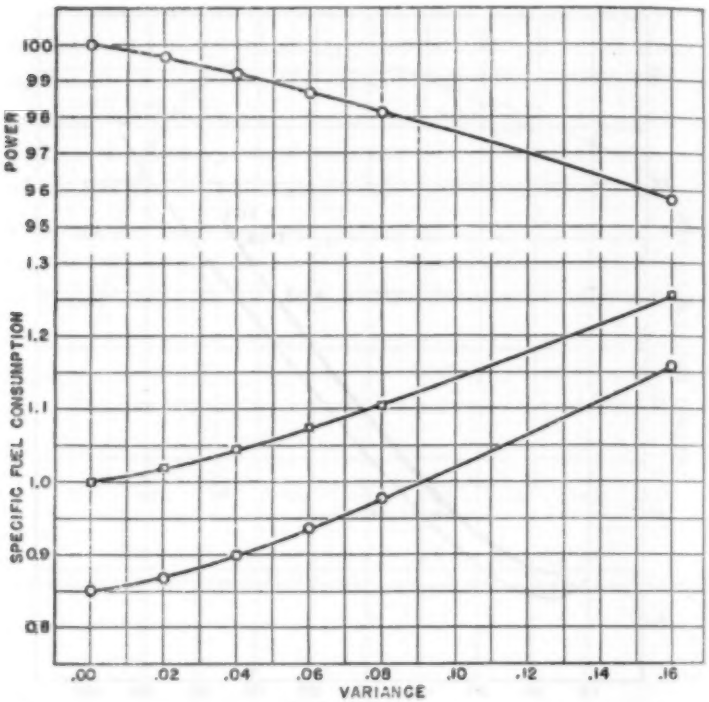

FIGURE 8.—*Effect of variance of distribution on engine performance.*

Lower curve is minimum specific fuel consumption. Middle curve is specific fuel consumption at maximum power. Variance is defined by eq 6.

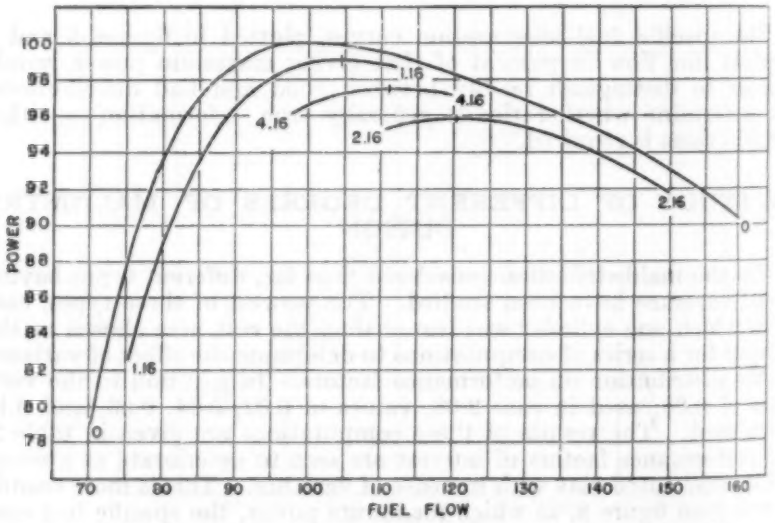

FIGURE 9.—*Power curves for three distributions of equal and high variance.*

Best performance results when the variance arises from one cylinder being rich (case 1.16); the poorest, when one cylinder is lean (case 2.16). One cylinder rich and one equally lean (case 4.16) gives intermediate performance.

TABLE 2.—*Effect of variance of distribution on performance*

[One cylinder lean, remainder rich]

1. Case number	0	2.02	2.04	2.06	2.08	2.16
2. Variance [a]	.00	0.02	0.04	0.06	0.08	0.16
3. Relative fuel to lean cylinder	1.000	.871	.817	.776	.742	.635
4. Relative fuel to each rich cylinder	1.000	1.026	1.037	1.045	1.052	1.073
5. Maximum power	100.00	99.64	99.18	98.68	98.13	95.74
6. Fuel flow for maximum power	100.0	101.6	103.6	105.9	108.5	120.2
7. Specific fuel consumption at maximum power	1.000	1.020	1.045	1.073	1.105	1.256
8. Minimum of curve of specific fuel consumption [b]	0.851	(0.864)	(0.879)	(0.897)	(0.917)	(1.018)
9. Minimum specific fuel consumption in firing range	.851	.867	.899	.937	.978	1.159
10. Fuel flow at minimum of specific fuel consumption curve	77.0	77.8	78.6	79.6	80.7	87.1
11. Minimum fuel flow to fire	70.0	80.4	85.6	90.2	94.4	110.3
12. Maximum fuel flow to fire	160.0	156.0	154.4	153.2	152.1	149.1
13. Firing-range ratio	2.29	1.94	1.80	1.70	1.61	1.35

[a] See eq 6.
[b] Parentheses indicate value lies outside firing range.

Computations were made for a total variance of 0.16 for two other types of distribution: case 1, in which one cylinder is richer than the rest; and case 4, in which one cylinder is leaner and another cylinder is equally richer than the rest. With so high a variance, the power curves, figure 9, are sharply differentiated and show clearly the differences in behavior accompanying these different types of distribution.

In endeavoring to select a criterion for the practical estimation of distribution quality and for the detection of changes therein, a number of factors were investigated. These included ratio of fuel flow at lean misfire to flow for maximum power, ratio of powers at these fuel flows, and product of the ratios of power at lean and at rich misfire to maximum power. Maximum power, specific fuel consumption at maximum power, and minimum specific fuel consumption for the various distributions were plotted against each of these factors. None of these, however, gave as good a correlation as was obtained by plotting the first two of the variables against minimum specific fuel consumption, figure 10. The latter value, directly determinable by test, is either the minimum of the specific fuel consumption curve, if this is reached, or the value reached at lean misfire, if the minimum has not then been attained.

It can be seen from figure 10 that maximum power and its attendant specific fuel consumption are well correlated with the value of minimum specific fuel consumption. This readily observable variable thus is shown to be a satisfactory index of distribution quality. Furthermore, a 1-percent change in maximum power is evidenced by a 5-percent change in minimum specific fuel consumption, showing that the latter is a good criterion for the former.

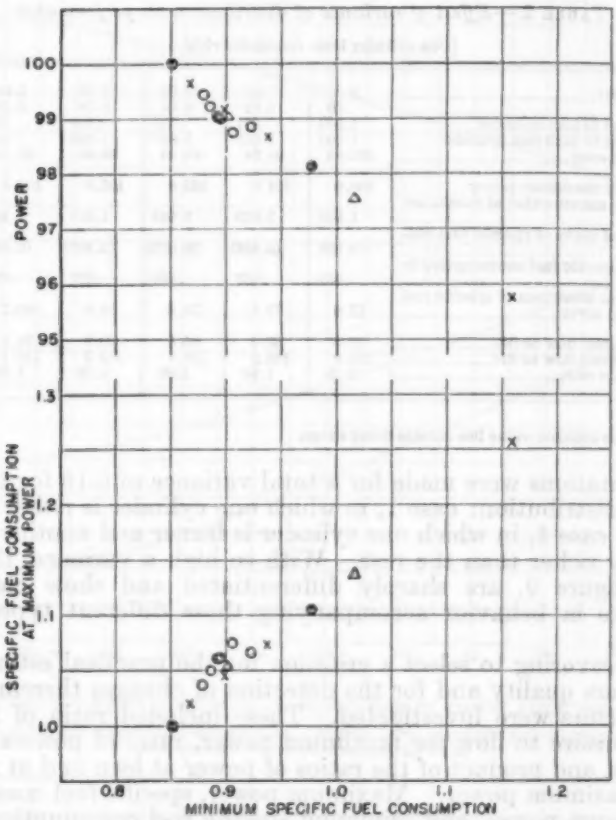

FIGURE 10.—*Correlation of maximum power and specific fuel consumption at maximum power with minimum specific fuel consumption.*

Minimum specific fuel consumption is seen to be a good criterion of distribution. Circles indicate cases 1 to 7 with a variance of 0.08; triangles, cases 1.16 and 4.16; crosses, case 2 with variance of 0.00 to 0.16.

V. ESTIMATION OF IMPROVEMENT ATTAINABLE

It has been shown in the foregoing sections that a change in distribution that improves engine performance in general is accompanied by an improvement in minimum specific fuel consumption. In weighing the advisability of further effort toward manifold improvement, it is desirable to know how much additional improvement is attainable in a given case. This can be determined by the methods given earlier, provided the actual distribution is measured by any appropriate means.

In the research on substitute fuels, a six-cylinder engine was operated on 190-proof alcohol, under normal operating conditions. The mixture distribution was determined by the use of thermocouple spark plugs, as described by Rabezzana and Kalmar [6]. The relative amount of fuel reaching each cylinder is shown by the value of X in the subsequent tabulation.

To determine the improvement in performance that might be expected with optimum manifolding, values of

$$\frac{\Sigma_1^6 f(X)}{6}$$

are first determined as follows:

Cylinder No.	X	$1/X$	log X	X^3
1	0.764	1.3089	−0.11691	0.5837
2	1.094	0.9141	+.03902	1.1968
3	1.069	.9355	+.02898	1.1428
4	1.046	.9560	+.01953	1.0941
5	1.214	.8237	+.08422	1.4738
6	0.813	1.2300	−.08991	0.6610
$\frac{\sum_1^6 f(X)}{6}$	1.000	1.0280	−.005845	1.0254

The performance equation is then formed, as in the example given earlier by the substitution of

$$x\frac{\sum_1^6 f(X)}{6}$$

for x in eq 2:

$$y=-\frac{136004.4}{x}-(7338.108 \log x-42.891)+ 13884.716+25.651x-0.035950x^2. \quad (7)$$

The derivatives of the performance equation and of the specific fuel consumption equation are also formed:

$$dy/dx=\frac{136004.4}{x^2}-\frac{3186.9}{x}+25.651-0.071900x \quad (8)$$

$$\frac{d(x/y)}{dx}=\frac{\frac{-272008.8}{x}-7338.108 \log x+17114.51+0.035950x^2}{y^2}. \quad (9)$$

The fuel consumption at which maximum power occurs is obtained by evaluating eq 8 at a series of values of x in the probable range:

x	dy/dx
109	+0. 023
110	+. 010
111	−. 002

From this tabulation, it is seen that the maximum power ($dy/dx=0$) occurs at $x=110.8$.

The leanest cylinder, no. 1, has a relative fuel flow of 0.764. It will misfire when the actual fuel flow to it reaches 70, or at an engine fuel flow of 70/.764 or 91.6. At this value of x, the numerator of eq 9 equals +49.99, indicating that the specific fuel consumption is increasing with fuel flow at this point. The minimum specific fuel

consumption therefore occurs at $x=91.6$, the point of lean misfire. Had eq 9 yielded a negative value, the point of minimum specific fuel consumption would be at a higher value of x, and would be found by the substitution of successive values of x, as was done above in the case of eq 8. The (interpolated) value of x causing eq 9 to equal zero would then be the fuel flow for minimum specific fuel consumption.

The values of x at which minimum specific fuel consumption and maximum power are attained, are next substituted in eq 7, to obtain the power at these values. From these results, the specific fuel consumptions at these points are computed. These values, in comparison with those for perfect distribution (case 0), were:

	Minimum specific fuel consumption		Maximum power	
	Example	Case 0	Example	Case 0
x (fuel flow)	91.6	77.0	110.8	100.0
y (power)	94.2	90.5	97.8	100.0
x/y (specific fuel consumption)	0.972	0.851	1.132	1.000

In the example in question, therefore, optimum manifolding would result in 2-percent gain in maximum power, and in over 10-percent gain in fuel economy.

VI. FACTORS NOT CONSIDERED IN ANALYSIS

It will be noted that the matter of spark advance has not been mentioned thus far. In the single-cylinder-engine tests on which this analysis is based the spark advance was optimum at each mixture ratio employed. This condition cannot be duplicated in a multicylinder engine, except in the case of perfect distribution. The different fuel-air mixtures reaching the several cylinders would require different spark advances for optimum performance. A study of this matter indicates, however, that the departure from the curves given herein will be inappreciable, except at very lean or very rich mixtures. If a fixed spark advance is used in multicylinder operation, as is customary, the power curves will be shortened and will be lower at lean and at rich mixtures than those shown herein.

It has also been tacitly assumed in this analysis that the variance of a distribution is the same at all mixture ratios. Actually, this is not the case. Vaporized fuel is distributed fairly evenly to all cylinders. The variance of a distribution arises almost entirely from maldistribution of liquid fuel. At richer mixture ratios, an increasing percentage of the fuel remains unvaporized. Hence the variance of distribution, for a given engine and fuel, tends to increase at richer mixture ratios. If the variance of distribution as discussed herein be assumed to apply at the lean end of the power curve, the effect of this factor can be roughly approximated by rotating the power curve clockwise about the lean end. Neither this effect nor that of departure of spark advance from optimum for the individual cylinders will invalidate the correlation shown in figure 10.

VII. CONCLUSIONS

The effects on engine performance of typical cases of maldistribution of the fuel-air mixture have been evaluated analytically from single-cylinder-engine test data. It has been shown that minimum specific fuel consumption is a good index of distribution, improvement in this variable generally being accompanied by improvement in the other engine-performance variables of interest. A method has been developed for ascertaining the attainable improvement over a given distribution.

VIII. REFERENCES

[1] Donald B. Brooks, J. Research NBS **35,** 1 (1945) RP1660.
[2] Jesse T. Duck and C. S. Bruce, J. Research NBS **35,** 439 (1945) RP1681.
[3] Stanwood W. Sparrow, NACA Technical Note 162 (1923).
[4] Donald B. Brooks, BS J. Research **3,** 795 (1929) RP118.
[5] D. B. Brooks, and E. A. Garlock, NACA Report 426 (1932).
[6] Hector Rabezzana and Stephen Kalmar, Automotive Ind. **66,** 450 and 486 (March 19 and 26, 1932).

WASHINGTON, January 5, 1946.

689974—46——3

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1713

Part of Journal of Research of the National Bureau of Standards, Volume 36, May 1946

EFFECTS OF MILDEW ON VEGETABLE-TANNED STRAP LEATHER

By Joseph R. Kanagy, Arbelia M. Charles, Edward Abrams, and Rees F. Tener

ABSTRACT

Samples of vegetable-tanned strap leather were exposed to conditions favorable for mildew growth in a tropical room at Fort Belvoir, Va., and in soil burial beds and in a humidity cabinet at the National Bureau of Standards. Mildew under these conditions varied from moderate to very heavy growth.

Physical tests showed that the growth of mildew on leather increased its stiffness, caused a loss in tensile strength, decreased stretch at the breaking point, and weakened the grain surface. Chemical tests revealed a loss of grease, water solubles, glucose, tannins, and nontannins.

No appreciable deterioration of the hide substance was indicated by the tests. The change in physical properties appeared to be due to the mildew activity impairing principally the outer surface of the leather.

The molds in assimilating the grease bring about decomposition (decarboxylation) of the fatty acids. This is shown by a decrease in the saponification number.

Samples of leather containing a fungicidal oil having as active ingredients a mixture of paranitrophenol and pentachlorophenol in equal proportions and aged under the same conditions as the untreated leathers showed no evidence of mildew after 12 weeks.

CONTENTS

	Page
I. Introduction	442
II. Experimental procedure	442
1. Selection and sampling of leathers	442
2. Preparation of samples for exposure tests	443
3. Conditions of exposure tests	444
(a) Soil burial	445
(b) Tropical room	445
(c) Humidity cabinet	445
4. Laboratory methods	445
(a) Preparation of specimens for testing	445
(b) Chemical analyses	445
(c) Physical tests	446
III. Results	446
1. Observation of exposed leathers	446
(a) Soil burial	446
(b) Tropical room	447
(c) Humidity cabinet	447
2. Chemical analyses	447
3. Physical tests	449
(a) Tensile strength	449
(b) Stretch at breaking point	449
(c) Change in stiffness	449
(d) Flexural fatigue	451
IV. General discussion	452
V. Summary	454

I. INTRODUCTION

Mildew growth on leather is a very common occurrence in the tropics, and accordingly the war in the South Pacific has created an unusual interest in this subject. Several fungicidal formulas for the prevention of the growth of mildew on leather have been developed by the National Bureau of Standards at the request of the Office of the Quartermaster General. This work has suggested a study of the actual damaging effects of these microorganisms on the leather other than those of changes in appearance and psychological effects on the observer.

A survey of the literature[1] disclosed studies of the stains produced on hides and leathers and a number of observations on the growth of mildew on leather-making materials. No data to show the effects of mildew on the physical and chemical properties of leather were found.

This report gives the results of an investigation on the effect of mildew on the physical and chemical properties of vegetable-tanned strap leather. The study was made on leathers exposed under controlled conditions varying from mild to severe, when judged on the basis of the rate of growth of mildew.

II. EXPERIMENTAL PROCEDURE

1. SELECTION AND SAMPLING OF THE LEATHERS

Seven vegetable-tanned strap-leather backs were selected for this work. Six of these were used for experiments in soil burial and in the tropical storage room. The other back was used to ascertain results in the humidity cabinet.

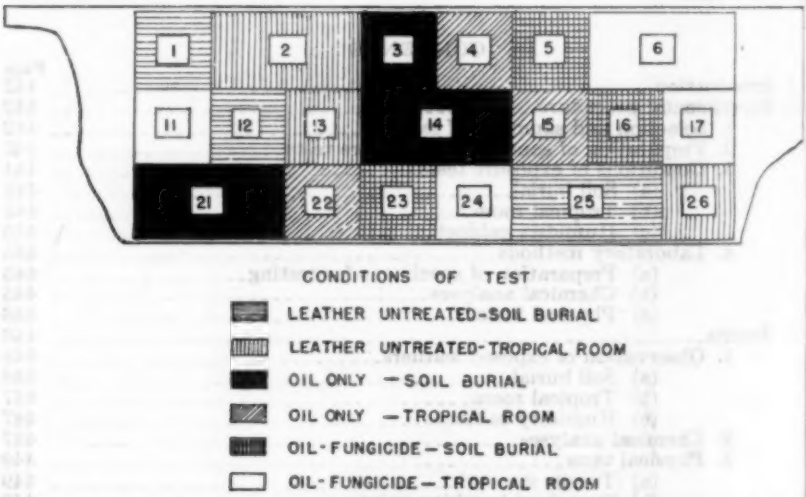

FIGURE 1.—*Method of sampling vegetable-tanned strap-leather backs for tests in soil burial and tropical room.*

Numbers 7 to 10, inclusive, and 18 to 20, inclusive, are omitted.

[1] J. Int. Soc. Leather Trades Chem. **9**, 274 and 355 (1925); **18**, 233 (1934); **19**, 153 (1935). J. Am Leather Chem. Assn. **24**, 657 (1929).

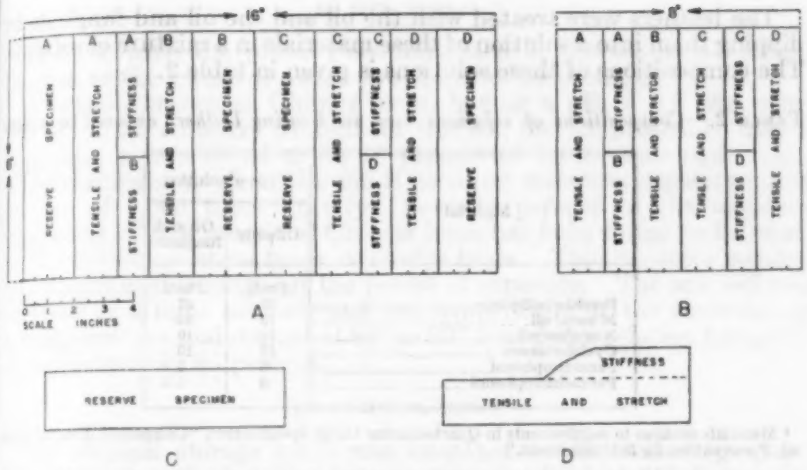

FIGURE 2.—*Method of cutting the pieces from the leather samples for the tests.*

A, Large sample; *B*, small sample; *C*, reserve specimen; *D*, piece exposed to mildew-growing conditions and from which specimens for tensile strength and stretch at break and stiffness determinations were cut.

Six different tests were made with the six backs. The backs were cut so as to obtain uniform sampling for each of the tests. The method adopted for sampling is illustrated in figure 1. The sample series for each test was rotated for each hide, so that each test contained samples from every location shown in figure 1.

The samples measured 16 by 8 inches and 8 by 8 inches. The method of dividing the samples is shown in figure 2. Four sets of pieces were cut from each sample.[2] One set was used as a control; the others for exposure to mildew.

The back used for the tests in the humidity cabinet was divided into 24 samples 8 by 8 inches. These were separated into two sets by alternate selection for two different tests. Each sample was cut into four sets of pieces, as described above.

2. PREPARATION OF SAMPLES FOR EXPOSURE TESTS

Information concerning treatment and exposure conditions for samples cut from the six backs of vegetable-tanned strap leather is given in table 1.

TABLE 1.—*Leather treatments and exposure conditions*

Test No.	Leather treatment	Exposure condition
1	Untreated	Soil burial.
2	do	Tropical room.
3	Oil only	Soil burial.
4	do	Tropical room.
5	Oil and fungicide	Soil burial.
6	do	Tropical room.

[2] No results are given in this paper for tests on the reserve specimens. The specimens are being held for future reference.

The leathers were treated with the oil and the oil and fungicide by dipping them into a solution of these materials in a mixture of solvents. The compositions of these solutions is given in table 2.

TABLE 2.—*Compositions of solutions used in treating leathers exposed to mildew*

Material [1]	Type of solution	
	Oil only	Oil and fungicide
	Parts	*Parts*
Perchlorcethylene	67	67
Mineral oil	10	10
Neatsfoot oil	10	10
Cyclohexanone	10	10
Paranitrophenol	0	1.5
Pentachlorophenol	0	1.5

[1] Materials conform to requirements in Quartermaster Corps Specification, "Compound, Leather Dressing, Preservative, for field treatment."

The two tests in the humidity cabinet were made with leathers dipped in the oil preparation and of other leathers dipped in the oil with fungicide preparation. The amounts of oil added to the leathers varied from 6.5 to 7.0 percent, whereas the total of the two fungicides varied from 0.85 to 0.90 percent. Unpublished data show that this fungicidal formula is effective for at least 30 days with as little as 0.2 percent of the fungicides in the leather. This material has been used for the treatment of shoes and other leather goods at a concentration of approximately 0.5 percent with no evidence of toxicity. It is, however, not recommended for use where direct contact is made with the skin.

The pieces of leather being treated were allowed to dry in a room (having uncontrolled weather conditions) until most of the solvent had evaporated. They were then placed in a conditioning room at 70° F and 65-percent relative humidity for 96 hours to allow the remainder of the solvent to evaporate and permit the establishment of equilibrium with the controlled atmosphere. Equilibrium was assumed when the weights of the pieces did not change more than 0.3 percent on two successive weighings 24 hours apart. The final weight was recorded for the determination of the amounts of oil and fungicide absorbed. One piece from each sample was selected for control, whereas the others were used in the exposure tests. These leather samples were exposed for periods of 4, 8, and 12 weeks under each of the conditions described in the following section.

3. CONDITIONS OF EXPOSURE TESTS

The conditions of soil burial as used at the National Bureau of Standards for the testing of textiles and a tropical room [3] at Fort Belvoir, Va., were selected for making the initial tests because from experience it was known that these conditions induced a heavy growth of mildew. The humidity cabinet was selected to represent surroundings where the growth of mildew was only moderate.

[3] T. F. Cooke and R. E. Vicklund, Ind. Eng. Chem. Anal. Ed. 18, 59 (1946).

(a) SOIL BURIAL

In these tests the pieces were imbedded in the soil in a vertical position to the extent of about two-thirds of their length.

A topsoil, known as Chester loam, having a pH of 5.0 was used. The optimum moisture content for this soil for the growth of microorganisms is considered to be 70 percent of its moisure equivalent. The moisture equivalent of a soil is its water retention capacity under a force of 1,000 times gravity. Seventy percent of the moisture equivalent of this sample of Chester loam has been found to be equal to 25 percent moisture on an oven-dry basis. This moisture content was maintained throughout the period of exposure. The soil bed was enclosed in a tight cabinet, and the temperature of the surrounding atmosphere was maintained at 85° to 90° F and at a relative humidity of approximately 95 percent.

(b) TROPICAL ROOM

The tropical storage room was operated on the following cycle: For 18 hours each day, the temperature was held at 85° F and the relative humidity at 90 percent. During the remaining 6 hours, the temperature was lowered to 75° F, and the humidity was raised to 95 to 100 percent. Condensation occurred on the leather samples during the 6-hour period. The leather was suspended, by means of wire, from a glass rod supported on a shelf at the sides of the room.

(c) HUMIDITY CABINET

This cabinet was maintained at 85° and 90° F and at a relative humidity of approximately 95 percent. The pieces were held by means of glass thread tied to a wooden rod that was placed in the uppermost of the cabinet.

4. LABORATORY METHODS

(a) PREPARATION OF SPECIMENS FOR TESTING

When the pieces of leather were removed from the different exposure conditions, they were dried under uncontrolled conditions. Mildew and soil were removed by rubbing the leather with a dry scrubbing brush. The pieces were then conditioned at 70° F and 65-percent relative humidity. After equilibrium was reached, as determined by maintenance of constant weight for 24 hours, specimens for tensile strength, stretch at the breaking point, and determinations of stiffness were cut from the exposed pieces of leather.

(b) CHEMICAL ANALYSES

The tensile-strength specimens, after being broken, were ground in a Wiley mill, thoroughly mixed, and used in making the chemical investigation.

This included a complete chemical analysis by the methods described in the Federal Specification KK-L-311, for Leather and Leather Products; General Specifications (Methods of Sampling, Inspection, and Tests). In addition, determinations of iodine and saponification

numbers were made on the greases,[4] and estimations of ammonia and soluble nitrogen were made on the leather to determine if any breakdown of the protein occurred.

The saponification number was determined by method 321.2 in Federal Specification KK–L–311. The iodine number was determined by the Wijs method (Methods of Analysis of the Association of Official Agricultural Chemists). Ammonia was determined by extracting 5 g of the leather with 200 ml of a solution of hydrochloric acid (0.05 *N*) by shaking the mixture in a bottle for 4 hours. One hundred milliliters of the filtered extract was placed in a Kjeldahl flask, sufficient magnesium oxide was added to make the solution alkaline, and the extracted ammonia was determined by distilling it into standardized acid.

Soluble nitrogenous materials were determined by extracting 2 g of the leather in 200 ml of sodium carbonate solution (0.1 *N*) by shaking the mixture in a bottle for 4 hours. The extract was filtered and the total nitrogen was determined on a 100 ml portion of the filtrate by method 350.1 in Federal Specification KK–L–311.

(c) PHYSICAL TESTS

Determinations of tensile strength and stretch at the breaking point were made in accordance with method 240.1 in Federal Specification KK–L–311.

Stiffness was determined in accordance with method 250.1 in the same specification. The relative stiffness factor was calculated for an angle of 20 degrees and a span of 2 inches.

Specimens previously used in the stiffness measurements were employed for the flexural fatigue tests. The fatigue machine was the one described by M. Maeser.[5] In order to accelerate the test, the method was modified however, by drilling a hole ($\frac{5}{16}$ inch) in the middle of the cross section where the specimen is notched. The end point was recorded when a crack was formed all the way across one of the two sections formed by the drilled hole and the notches.

III. RESULTS

1. OBSERVATION OF EXPOSED LEATHERS

(a) SOIL BURIAL

Within 2 days after exposure a heavy white mycelium was noticed on the exposed portion of the oil-treated leather. By the end of the first week this had developed into a uniform black coating of Aspergillus niger, and at the end of the first 4 weeks a very heavy coating of this mold was present. No other organism manifested itself at this time. At the end of the second and third exposure periods, the exposed portions of the oil-treated specimens showed luxuriant growths of Aspergillus niger, with an overgrowth of an olive green Penicillium.

The specimens that contained no added oil showed a slight growth of Aspergillus niger; but in this case various species of Penicillium were also present, along with a strain of Aspergillus oryzae. At the end

[4] Includes added oils and original stuffing mixture.
[5] J. Am. Leather Chem. Assn. **39**, 35 (1944).

of 12 weeks of exposure, an increased amount of growth of a variety of organisms was evident, but the underlying surface of the leather was still partly visible.

The portions of the specimens treated with fungicide that were exposed above ground showed no evidence of growth even after 12 weeks of exposure.

The buried portions of these specimens showed little or no growth. However, a few colored spots which are believed to have been of bacterial origin were noticed on the buried portions of all pieces, including those treated with fungicide.

(b) TROPICAL ROOM

The types of mold on the specimens in the tropical room were similar to those on the portions of the samples that were above ground in the soil-burial tests. The molds were also more abundant in the tropical room than in the burial tests, but there was no evidence of spots similar to those on the buried portions in the soil-burial tests.

The samples treated with the fungicides showed no evidence of growth at any time. There were droplets collected at the bottom of the specimens, however, and there was some evidence of spue on the surface of those having the highest precentage of water-soluble materials.

(c) HUMIDITY CABINET

Mildew-growth on the leather under the conditions of the humidity cabinet was only of moderate extent. The grain side of the leather was almost completely covered with a moderate growth of Aspergillus niger, whereas the flesh surface was sparsely covered with a slight growth of this mold.

2. CHEMICAL ANALYSES

In table 3 are given analyses of the composite samples used in the soil-burial and tropical-room tests, together with the results of tests applied to the greases and the determinations of soluble nitrogen compounds. Also included are similar analyses after the various exposure periods; and, in addition, the analytical results of similar tests applied to leathers exposed in the humidity cabinet.

Differences due to exposure conditions rather than to the effect of mildew are reflected in the results of the chemical analyses. The leathers exposed to soil burial showed increases in ash and pH value. The ash increase is undoubtedly caused by pickup from the soil since, as shown, the ash contained calcium and magnesium salts.

The leathers exposed to the tropical room absorbed ammonia from an accidentally contaminated atmosphere. This resulted in an increase in pH and in the hydrolysis of some of the tanning material, as shown by the increase in water solubles and tannins.

The leathers not treated with fungicides showed a large decrease in percentage of grease. Samples containing fungicide showed small grease losses, which may be attributed to adsorption of grease by the soil for the soil-burial samples, and possibly to leaching for the tropical-room and humidity-cabinet samples.

Leathers treated with fungicides and exposed in the humidity cabinet showed considerable losses in water-soluble materials.

689974—46——4

TABLE 3.—*Chemical analyses of leather used in mildew study*

Conditions of tests	Time of exposure	Moisture	pH	Ash	Grease, hide-substance basis	Grease	Hide substance	Water solubles	Degree of tannage	Non-tannins	Tannins	Glucose	Magnesium sulfate[1]	Calcium oxide	Iodine number	Saponification number	Nitrogen[2] extraction with HCl solution	Nitrogen[3] extraction with Na_2CO_3 solution
	Weeks	*Percent*		*Percent*	*Percent*	*Percent*	*Percent*	*Percent*		*Percent*	*Percent*	*Percent*	*Percent*	*Percent*			*Percent*	*Percent*
Leather untreated; soil burial	0	13.2	3.4	0.67	12.8	6.4	50.4	11.2	63	3.4	7.8	0.78	0.65	Trace	54	186	0.06	0.20
	4	13.3	3.6	1.18	8.3	4.0	51.7	8.4	69	3.0	5.4	.40	.60	0.26	73	163	.08	.24
	8	15.6	3.6	1.16	6.5	3.3	51.6	7.7	72	3.0	4.7	.58	.87	.28	70	83	.03	.26
	12	15.6	3.9	1.39	5.3	2.8	52.8	7.2	70	3.0	4.2	Trace	1.06	.27	71	113	.05	.30
Leather untreated; tropical room	0	13.2	3.4	0.67	12.8	6.4	50.4	11.2	63	3.4	7.8	0.78	0.65	Trace	54	186	.06	.20
	4	14.6	5.9	.59	7.9	4.3	55.0	17.0	43	4.1	12.9	.30	.65	Trace	69	175	.31	.82
	8	18.4	6.3	.59	5.0	2.9	57.7	14.8	42	4.3	10.5	Trace	.65	Trace	68	99	.70	.86
	12	17.7	6.3	.57	4.3	2.5	59.0	8.8	50	2.7	6.1	Trace	.65	Trace	72	111	.71	.85
Oil only; soil burial	0	12.3	3.4	.58	25.4	13.4	46.3	10.6	64	3.0	7.6	0.94	.49	Trace	61	147	.05	.09
	4	13.0	3.7	.94	15.9	8.1	51.0	8.6	63	2.8	5.8	.68	.26	0.18	61	97	.10	.31
	8	15.7	3.8	1.16	13.0	6.9	53.0	7.7	61	2.5	5.2	.48	.85	.27	55	67	.03	.23
	12	15.6	4.0	1.33	12.1	6.5	53.7	7.3	60	2.9	4.4	.12	1.34	.31	50	55	.05	.32
Oil only; tropical room	0	12.2	3.4	0.63	27.9	12.9	46.1	10.9	65	3.1	7.8	1.08	0.44	Trace	61	144	.05	.04
	4	13.9	5.9	.60	19.9	10.3	52.0	16.9	40	4.0	12.9	0.64	.44	Trace	59	118	.50	.81
	8	18.1	6.2	.51	15.4	8.5	55.2	14.6	39	4.0	10.6	.48	.44	Trace	58	92	.60	.84
	12	17.7	6.3	.56	10.8	6.2	57.5	11.1	44	3.0	8.1	.12	.44	Trace	53	60	.06	.81
Oil and fungicide; soil burial	0	10.2	3.5	.58	28.7	13.4	46.7	10.3	63	3.0	7.3	.76	.41	Trace	59	141	.06	.17
	4	11.9	3.3	.81	31.5	14.8	47.0	7.6	65	1.9	5.7	.76	.41	0.20	66	139	.09	.25
	8	14.1	3.5	1.06	26.7	13.1	48.6	6.6	65	1.9	4.7	.20	.57	.33	66	121	.03	.25
	12	14.9	3.7	1.25	24.0	11.9	49.6	5.7	66	2.4	3.3	.14	1.47	.34	63	114	.05	.33
Oil and fungicide; tropical room	0	11.9	3.5	0.57	29.0	13.5	46.5	10.4	63	3.0	7.4	.80	0.43	Trace	63	142	.04	.24
	4	12.8	6.0	.49	30.6	14.9	48.7	16.5	41	4.3	12.2	.42	.43	Trace	71	150	.49	.69
	8	16.2	6.2	.47	30.1	15.4	50.5	16.2	35	4.1	12.1	.46	.52	Trace	67	123	.90	.75
	12	15.4	6.2	.45	28.9	14.1	52.2	14.1	37	3.3	10.8	.08	.43	Trace	64	131	.63	.84
Oil only; humidity cabinet	0	13.4	3.2	2.48	40.7	14.8	36.3	16.4	89	7.5	8.9	1.96	2.41	0.04	96	102	0.05	0.24
	4	13.1	3.1	1.54	36.6	14.0	38.2	12.8	91	4.0	8.8	0.04	2.06	.04	94	107	.04	.23
	8	15.0	3.1	1.66	33.6	12.4	40.0	12.6	87	4.7	7.9	Trace	2.21	.06	100	80	.02	.24
	12	15.9	3.2	1.34	29.7	12.4	41.7	10.8	84	3.4	7.4	0.08	1.38	.05	96	66	.03	.24
Oil and fungicide; humidity cabinet	0	13.0	3.3	2.25	43.8	15.5	35.3	17.8	89	8.3	9.5	2.28	3.24	.04	92	116	.05	.24
	4	13.9	3.3	1.23	39.7	15.1	38.0	12.7	90	4.5	8.2	1.94	1.27	.04	92	121	.04	.25
	8	15.3	3.3	0.75	37.8	13.2	40.6	10.6	83	2.8	7.8	0.92	1.37	.05	94	105	.05	.26
	12	13.6	3.3	0.73	37.8	13.2	41.6	9.0	83	2.8	6.8	.59	0.79	.05	91	113	.03	.26

[1] Magnesium sulfate was added to the solutions in which the leather was tanned.

[2] Nitrogen extraction with HCl solution is a measure of the amount of hide substance.

[3] Nitrogen extraction with Na_2CO_3 solution is a measure of the amount of hide substance plus the amount of tannin.

PERCENTAGE LOSS IN TENSILE STRENGTH

3. PHYSICAL TESTS

(a) TENSILE STRENGTH

The results of tensile-strength tests are given in figure 3. Mildewed leathers (not treated with fungicides) showed greater losses in tensile strength than those treated with fungicides. After the first 4 weeks, the samples exposed to soil burial and in the humidity cabinet lost tensile strength at a lower rate than those exposed in the tropical room.

The buried fungicide-treated leathers developed greater losses in tensile strength for the 12-week period than similar specimens exposed in either the tropical room or the humidity cabinet for the

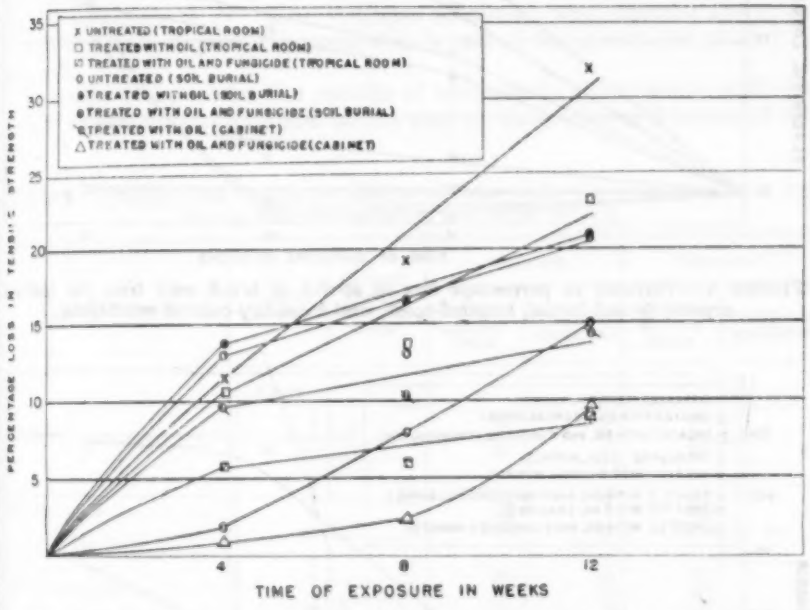

FIGURE 3.—*Increase in percentage loss in tensile strength with time for leathers exposed to soil-burial, tropical-room, and humidity-cabinet conditions.*

same time period. This may have been the result of conditions in the soil.

(b) STRETCH AT BREAKING POINT

The percentage loss in stretch at the breaking point (fig. 4) correlates well with the results of the tensile-strength tests (fig. 3), with the exception of the humidity-cabinet tests. These showed no appreciable change in loss of stretch before the 12-week exposure period.

(c) CHANGE IN STIFFNESS

The results of the stiffness measurements are plotted in figure 5. All the curves cut the ordinate at a relative stiffness-factor value of 190, since this was the average result for all the control specimens.

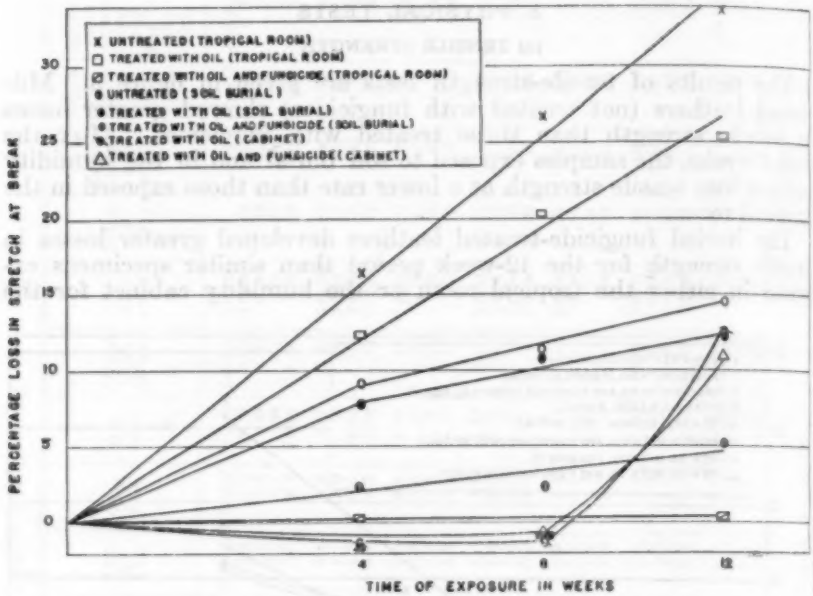

FIGURE 4.—*Increase in percentage loss in stretch at break with time for leathers exposed to soil-burial, tropical-room, and humidity-cabinet conditions.*

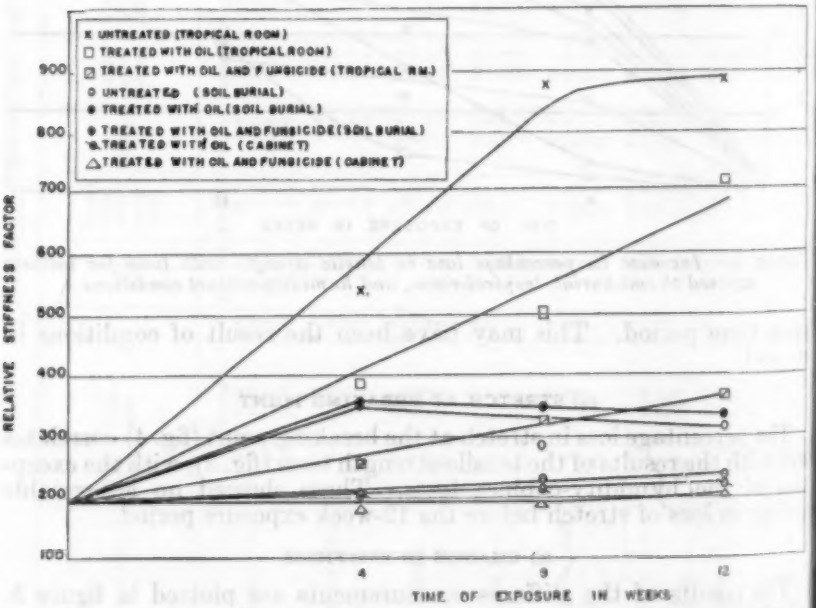

FIGURE 5.—*Increase in relative stiffness factor with time for leathers exposed to soil-burial, tropical-room, and humidity-cabinet conditions.*

All the leathers that had a growth of mildew showed greater increases in stiffness than the exposed specimens treated with fungicides and had no growth of mildew. The samples exposed to soil burial showed decreasing stiffness values after the first 4 weeks of exposure. This may have been caused by the slow redistribution of grease from the interior to the surfaces of the leather. The surface of the leather had probably lost a considerable amount of grease during the first 4 weeks of underground storage because of close contact with the surrounding soil. After the first 4 weeks, the loss to the soil was less, and a redistribution of grease then took place in the leather.

Stiffness specimens were cut from portions of the soil-burial specimens that were either completely covered with soil or only partly submerged. This may be visualized from the diagram of the piece shown in figure 2, *D*. The stiffness specimen was exposed above or below the soil, depending upon which end of the piece was placed in the soil.

In table 4 are given the results of changes in the relative stiffness factor of specimens exposed above and of those exposed beneath the soil.

TABLE 4.—*Comparative change in relative stiffness factor*[1] *of specimens from soil burial tests exposed above and below the soil*

Leather treatment	Time of exposure	Control[2] relative stiffness factor	Above soil		Below soil	
			Relative stiffness factor	Number of specimens	Relative stiffness factor	Number of specimens
	Weeks					
Untreated	0	213				
	4		351	12	276	7
	8		291	12	356	7
	12		316	9	258	10
Oil only	0	177				
	4		354	10	278	9
	8		349	8	259	11
	12		337	11	227	8
Oil and fungicide	0	181				
	4		204	13	295	6
	8		225	10	270	9
	12		220	9	417	10

[1] Calculated at angle of 20 degrees and span of 2 inches.
[2] Average of 19 specimens.

These data show that leathers with mildew gradually increased in stiffness when aged above ground. Leathers without mildew increased in stiffness when exposed below the soil. These findings indicate that contact with soil increases the stiffness of leather, as might be expected. In this respect, however, mildew appears to be more effective than soil action.

(d) FLEXURAL FATIGUE

The results of flexural-fatigue tests for the leathers aged in the humidity cabinet are given in table 5. They show that there is considerably more tendency for the grain to crack on those that had supported mildew than on those that had no mildew growth.

TABLE 5.—*Resistance of leathers, exposed to mildew-growing conditions in humidity cabinet, to flexural fatigue in the Maeser machine*

Leather treatment	Time of exposure	Grain crack [1]	
		Started	Across specimen
	Weeks	*Flexes*	*Flexes*
Treated with oil only	8	28,080	[2] 41,570
	8	21,360	31,800
	12	15,740	27,240
	12	16,200	29,520
	12	15,310	20,300
Treated with oil and fungicide	12	[3]	[3]
	12	34,080	[2] 41,570
	12	33,890	36,860

[1] Machine runs through cycle having 41,570 flexes. Specimens were tested through only 1 cycle.
[2] Not completely across.
[3] No crack in first cycle.

IV. GENERAL DISCUSSION

The results of the tests give evidence that the growth of mildew on leather is supported by the greases, which act as a nutrient. Tests on the greases show a decrease in the saponification numbers, which indicates that the microorganisms attack the fatty acids at the

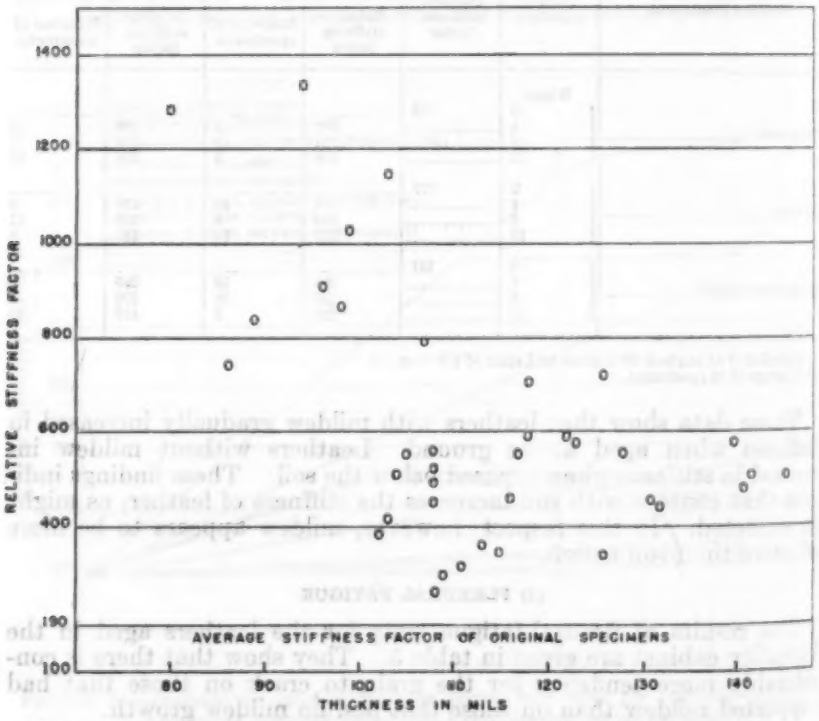

FIGURE 6.—*Variation of relative stiffness factor with thickness of the specimens.*

carboxyl group and decarboxylation apparently occurs. Iodine-number determinations give a possible indication of dehydrogeneration of fatty oils and the preferential assimilation of them. This is shown by an increase in iodine number where only fatty oils are present and a decrease in iodine numbers where mineral oil is also present.

It is not definitely proved by these results that the mildew assimilates the tannins. The leathers not treated with a fungicide and exposed to the tropical-room tests show larger decreases in tanning materials than those that were treated and did not support mildew growth, but apparently an indeterminable amount of this loss was caused by leaching.

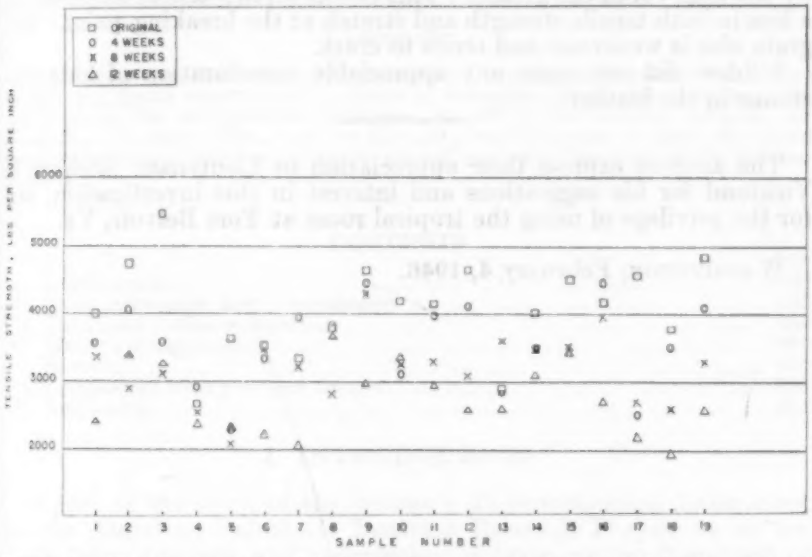

FIGURE 7.—*Tensile strengths of individual specimens of untreated leather exposed in the tropical room for 4, 8, and 12 weeks.*

As the growth of mildew occurs on the outer surface of the leather, it would be expected that the effect of the mildew would be most severe on the thinner leathers, which have the highest percentage of outer surface per unit weight. In figure 6 the relative stiffness factors of the specimens not treated with the fungicides and aged in the tropical room for 12 weeks are plotted against their thicknesses. The original specimens had relative stiffness factors varying from 70 to 380, with an average of 190. These results show that the thinner leathers have the greatest increases in stiffness.

Tests of the soluble nitrogenous materials in the exposed leathers, as determined by extracting with 0.1-*N* sodium carbonate solution, show that no appreciable deterioration of the hide substance has occurred. In figure 7 are shown the percentage losses in tensile strength of each specimen of leather that had been given no treatment and exposed to the tropical room. Only one of these speci-

mens has a final tensile strength of less than 2,000 pounds, even though the control specimen of some of these samples was not appreciably higher. This indicates further that no breakdown of the basic chemical structure of the hide substance has occurred and that the loss in tensile strength is principally caused by changes in the physical structure of the leather. The maintenance of chemical stability should prevent, as indicated, the reduction of tensile strength below some definite minimum value.

V. SUMMARY

The action of mildew on vegetable-tanned leather produces changes in its physical properties. These changes are caused, at least in part, by the removal of the grease. This causes an increase in stiffness and a loss in both tensile strength and stretch at the breaking point. The grain also is weakened and tends to crack.

Mildew did not cause any appreciable deterioration of hide substance in the leather.

The authors express their appreciation to Lieutenant Richard E. Vicklund for his suggestions and interest in this investigation, and for the privilege of using the tropical room at Fort Belvoir, Va.

WASHINGTON, February 4, 1946.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1714

Part of Journal of Research of the National Bureau of Standards, Volume 36, May 1946

HEATS OF COMBUSTION AND FORMATION AT 25° C OF THE ALKYLBENZENES THROUGH $C_{10}H_{14}$, AND OF THE HIGHER NORMAL MONOALKYLBENZENES[1]

By Edward J. Prosen, Walter H. Johnson, and Frederick D. Rossini

ABSTRACT

Values are given for the heats of combustion (in oxygen to form gaseous carbon dioxide and liquid water) and the heats of formation (from the elements, solid carbon (graphite) and gaseous hydrogen), at 25° C, for benzene, toluene, the four C_9H_{10}, the eight C_9H_{12}, and the 22 $C_{10}H_{14}$ alkylbenzenes, in both the liquid and gaseous states, and for the higher normal monoalkylbenzenes in the gaseous state.

CONTENTS

		Page
I.	Introduction	455
II.	Units, constants, and uncertainties	455
III.	Data used in the calculations	456
IV.	Method of calculation	456
V.	Results	458
VI.	Comparison with previous data	458
VII.	References	461

I. INTRODUCTION

As part of the work of the Bureau's Thermochemical Laboratory and the American Petroleum Institute Research Project 44 on the "Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons," this report presents values for the heats of combustion and of formation at 25° C of the alkylbenzenes through $C_{10}H_{14}$, in both liquid and gaseous states, and of the higher normal monoalkylbenzenes in the gaseous state.

II. UNITS, CONSTANTS, AND UNCERTAINTIES

The unit of energy upon which the values presented in this paper are based is the international joule determined by standards of resistance (international ohms), electromotive force (international volts), and time (mean solar seconds) maintained at this Bureau. Conver-

[1] This investigation was performed at the National Bureau of Standards jointly by the Thermochemical Laboratory and the American Petroleum Institute Research Project 44 on the "Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons."

689974—46——5

sion to the conventional thermochemical calorie is made by means of the relation [1][2].

4.1833 international joules = 1 calorie.

The atomic weights of hydrogen, oxygen, and carbon were taken as 1.0080, 16.0000, and 12.010, respectively, from the 1941 table of International Atomic Weights [2].

The uncertainties assigned to the various quantities dealt with were derived, where possible, by a method previously described [3]. In other cases, reasonable estimates of the uncertainty were made.

III. DATA USED IN THE CALCULATIONS

The data used in the calculations are the following:

Heat of formation of carbon dioxide at 25° C [4].

Heat of formation of water at 25° C [5].

Heats of combustion of benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, and *n*-propylbenzene, in the liquid state at 25° C [6].

Heats of combustion of isopropylbenzene, 1-methyl-2-ethylbenzene, 1-methyl-3-ethylbenzene, 1-methyl-4-ethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene, in the liquid state at 25° C [7].

Heats of combustion of *n*-butylbenzene, isobutylbenzene, *sec*-butylbenzene, and *tert*-butylbenzene, in the liquid state at 25° C [8].

Standard heats of vaporization at 25° C for benzene, toluene, the four C_8H_{10}, the eight C_9H_{12}, and the twenty-two $C_{10}H_{14}$ alkylbenzenes, from a correlation by Wagman, Taylor, Pignocco, and Rossini [9] of selected "best" values based largely on the experimental data on the heats of vaporization at 25° C of benzene, toluene, ethylbenzene, the three xylenes, the two propylbenzenes, and the three trimethylbenzenes by Osborne and Ginnings [10].

IV. METHOD OF CALCULATION

The selected values for the heats of combustion of the hydrocarbon in the liquid state at 25° C were taken as reported in reference [6] for benzene, toluene, ethylbenzene, the three xylenes, and *n*-propylbenzene, in reference [7] for isopropylbenzene, the three methylethylbenzenes, and the trimethylbenzenes, and from reference [8] for *n*-butylbenzene, isobutylbenzene, *sec*-butylbenzene, and *tert*-butylbenzene. The corresponding values for the heat of combustion of the hydrocarbon in the gaseous state at 25° C were obtained by appropriately adding the values of the heats of vaporization from reference [9].

The selected values for the heats of formation of the above hydrocarbons in the liquid and gaseous states at 25° C were obtained by appropriately combining the values of the heats of formation of water and carbon dioxide from references [4, 5] with the corresponding selected values for the heats of combustion.

The corresponding values for the higher normal monoalkylbenzenes were obtained by adding to the values for *n*-butylbenzene the appropriate increments per CH_2 group reported for the normal paraffin hydrocarbons above *n*-pentane [11].

[2] Figures in brackets indicate the references at the end of the paper.

The values for the heats of formation in the gaseous state at 25° C for all the $C_{10}H_{14}$ alkylbenzenes except the four butylbenzenes were calculated by a method involving the summing of contributions from component parts of the molecule (phenyl, methyl, ethyl, *n*-propyl, and isopropyl groups), together with contributions associated with the positions of the substituent groups on the benzene ring.[3] The necessary constants were evaluated by the method of least squares from the selected values of the heats of formation in the gaseous state at 25° C for toluene, ethylbenzene, *n*-propylbenzene, isopropylbenzene, the three xylenes, the three methylethylbenzenes, and the three trimethylbenzenes.

By this method, the heat of formation of an alkylbenzene hydrocarbon, with one phenyl group having methyl, ethyl, *n*-propyl, or isopropyl substituent groups, is taken as

$$n\mathrm{C(solid,\ graphite)}+(n-3)\mathrm{H_2(gas)}=\mathrm{C_nH_{2n-6}(gas)} \quad (1)$$

$$\Delta Hf^\circ_{298.16}=\beta_\phi+z_\mathrm{I}\beta_\mathrm{I}+z_\mathrm{II}\beta_\mathrm{II}+z_\mathrm{III}\beta_\mathrm{III}+z_{\mathrm{III}_i}\beta_{\mathrm{III}_i}+z_o\beta_o+z_m\beta_m+z_p\beta_p \text{ kcal/mole}, \quad (2)$$

where

z_I = the number of methyl groups

z_II = the number of ethyl groups

z_III = the number of *n*-propyl groups

z_{III_i} = the number of isopropyl groups

z_o = the number of ortho pairs of substituents (being, for example, one in *o*-xylene and two in 1,2,3-trimethylbenzene)

z_m = the number of meta pairs of substituents (being, for example, one in *m*-xylene and 1,2,3-trimethylbenzenes and three in 1,3,5-trimethylbenzene)

z_p = the number of para pairs of substituents (being, for example, one in *p*-xylene and two in 1,2,4,5-tetramethylbenzene)

β_ϕ = 19.383 kcal/mole, representing the contribution of the one phenyl group

β_I = −7.508 kcal/mole, representing the contribution of one methyl group

β_II = −12.190 kcal/mole, representing the contribution of one ethyl group

β_III = −17.513 kcal/mole, representing the contribution of one *n*-propyl group

β_{III_i} = −18.443 kcal/mole, representing the contribution of one isopropyl group

β_o = 0.469 kcal/mole, representing the contribution arising from each pair of substituent groups which are in ortho positions with respect to each other

β_m = −0.225 kcal/mole, representing the contribution arising from each pair of substituent groups which are in meta positions with respect to each other

β_p = −0.327 kcal/mole, representing the contribution arising from each pair of substituent groups which are in para positions with respect to each other.

[3] This method is similar to that previously used in reference [9] in the evaluation of the heats of vaporization of compounds for which no data exist.

The foregoing constants yield values of the heats of formation of the C_7H_8 to C_9H_{12} alkylbenzenes which differ from the selected best values by the following amounts, in kilocalories per mole: Toluene, −0.08; ethylbenzene, 0.07; *o*-xylene, 0.30; *m*-xylene, 0.02; *p*-xylene, −0.25; 1-methyl-2-ethylbenzene, −0.14; 1-methyl-3-ethylbenzene, −0.08; 1-methyl-4-ethylbenzene, 0.14; 1,2,3-trimethylbenzene, −0.14; 1,2,4-trimethylbenzene, 0.11; 1,3,5-trimethylbenzene, 0.02. As 0.12 kcal/mole is only 0.01 percent of the value of the heat of combustion of a C_9H_{12} alkylbenzene, the correlation is considered satisfactory.

The values calculated by the foregoing method for the $C_{10}H_{14}$ alkylbenzenes, except the four butylbenzenes, are believed to be uncertain by not more than about ±0.40 to ±0.70 kcal/mole, which is ±0.03 to ±0.05 percent of their heats of combustion.

V. RESULTS

In table 1 are presented the selected "best" values for the heats of combustion and formation at 25° C of the 36 alkylbenzenes through $C_{10}H_{14}$, in both the liquid and gaseous state, and for some higher normal monoalkylbenzenes in the gaseous state.

For the heats of combustion of the normal monoalkylbenzenes above *n*-propylbenzene, in the gaseous state at 25° C:

$$C_nH_{2n-6}(\text{normal alkylbenzene, gas})+(3/2)(n-1)O_2(\text{gas})=nCO_2(\text{gas})+(n-3)H_2O(\text{liq}) \quad (3)$$

$$-\Delta Hc^\circ_{298.16}=-158.990+157.443n\pm(0.4226-0.06556n+0.003428n^2)^{\frac{1}{2}}\ \text{kcal/mole};\ n>9 \quad (4)$$

Similarly, the heats of formation of the higher normal monoalkylbenzenes in the gaseous state at 25° C are:

$$n\text{C(solid, graphite)}+(n-3)H_2(\text{gas})=C_nH_{2n-6}(\text{normal alkylbenzene, gas}) \quad (5)$$

$$\Delta Hf^\circ_{298.16}=45.960-4.926n\pm(0.4234-0.06611n+0.003637n^2)^{\frac{1}{2}}\ \text{kcal/mole};\ n>9 \quad (6)$$

The foregoing equations incorporate the increment per CH_2 previously reported for the normal paraffin hydrocarbons [11].

VI. COMPARISON WITH PREVIOUS DATA

Comparison of previous experimental data with the selected best values from this report is shown in table 2, in which the values from earlier investigations have been converted, insofar as significant, to the present unit of energy and atomic weights.

TABLE 1.—*Selected "Best" values for the heats of combustion and formation of the Alkylbenzenes*

Compound	Formula	Heat of combustion [a] at 25° C, $-\Delta Hc°$		Heat of formation [b] at 25° C, $\Delta Hf°$	
		Liquid	Gas	Liquid	Gas
		kcal/mole	*kcal/mole*	*kcal/mole*	*kcal/mole*
Benzene	C_6H_6	780.98 ±0.10	789.08 ±0.10	11.72 ±0.12	19.82 ±0.12
Methylbenzene (toluene)	C_7H_8	934.50 ±0.12	943.58 ±0.12	2.87 ±0.15	11.95 ±0.15
Ethylbenzene	C_8H_{10}	1091.03 ±0.17	1101.13 ±0.17	−2.98 ±0.20	7.12 ±0.20
1,2-Dimethylbenzene (o-xylene).	C_8H_{10}	1088.16 ±0.24	1098.54 ±0.24	−5.84 ±0.26	4.54 ±0.26
1,3-Dimethylbenzene (m-xylene).	C_8H_{10}	1087.92 ±0.15	1098.12 ±0.15	−6.08 ±0.18	4.12 ±0.18
1,4-Dimethylbenzene (p-xylene).	C_8H_{10}	1088.16 ±0.22	1098.29 ±0.22	−5.84 ±0.24	4.29 ±0.24
n-Propylbenzene	C_9H_{12}	1247.19 ±0.16	1258.24 ±0.16	−9.18 ±0.20	1.87 ±0.20
Isopropylbenzene	C_9H_{12}	1246.52 ±0.23	1257.31 ±0.23	−9.85 ±0.26	0.94 ±0.26
1-Methyl-2-ethylbenzene	C_9H_{12}	1245.26 ±0.23	1256.66 ±0.25	−11.11 ±0.26	0.29 ±0.28
1-Methyl-3-ethylbenzene	C_9H_{12}	1244.71 ±0.26	1255.92 ±0.27	−11.67 ±0.28	−0.46 ±0.29
1-Methyl-4-ethylbenzene	C_9H_{12}	1244.45 ±0.32	1255.59 ±0.33	−11.92 ±0.34	−0.78 ±0.35
1,2,3-Trimethylbenzene	C_9H_{12}	1242.36 ±0.28	1254.08 ±0.28	−14.01 ±0.30	−2.29 ±0.30
1,2,4-Trimethylbenzene	C_9H_{12}	1241.58 ±0.24	1253.04 ±0.24	−14.79 ±0.27	−3.33 ±0.27
1,3,5-Trimethylbenzene	C_9H_{12}	1241.19 ±0.32	1252.53 ±0.32	−15.18 ±0.34	−3.84 ±0.34
n-Butylbenzene	$C_{10}H_{14}$	1403.46 ±0.27	1415.44 ±0.28	−15.28 ±0.30	−3.30 ±0.31
Isobutylbenzene	$C_{10}H_{14}$	1402.04 ±0.29	1413.59 ±0.31	−16.70 ±0.32	−5.15 ±0.34
sec-Butylbenzene	$C_{10}H_{14}$	1402.85 ±0.27	1414.57 ±0.30	−15.89 ±0.30	−4.17 ±0.33
tert-Butylbenzene	$C_{10}H_{14}$	1401.82 ±0.27	1413.32 ±0.31	−16.92 ±0.30	−5.42 ±0.34
1,2-Diethylbenzene	$C_{10}H_{14}$	1401.80 ±0.44	1414.21 ±0.42	−16.94 ±0.42	−4.53 ±0.40
1,3-Diethylbenzene	$C_{10}H_{14}$	1401.30 ±0.44	1413.52 ±0.42	−17.44 ±0.42	−5.22 ±0.40
1,4-Diethylbenzene	$C_{10}H_{14}$	1401.27 ±0.44	1413.42 ±0.42	−17.47 ±0.42	−5.32 ±0.40
1-Methyl-2-n-propylbenzene	$C_{10}H_{14}$	1401.22 ±0.53	1413.57 ±0.52	−17.52 ±0.51	−5.17 ±0.50
1-Methyl-3-n-propylbenzene	$C_{10}H_{14}$	1400.72 ±0.53	1412.88 ±0.52	−18.02 ±0.51	−5.86 ±0.50
1-Methyl-4-n-propylbenzene	$C_{10}H_{14}$	1400.68 ±0.53	1412.77 ±0.52	−18.06 ±0.51	−5.97 ±0.50
1-Methyl-2-isopropylbenzene	$C_{10}H_{14}$	1400.55 ±0.53	1412.64 ±0.52	−18.19 ±0.51	−6.10 ±0.50
1-Methyl-3-isopropylbenzene	$C_{10}H_{14}$	1400.05 ±0.53	1411.95 ±0.52	−18.69 ±0.51	−6.79 ±0.50
1-Methyl-4-isopropylbenzene	$C_{10}H_{14}$	1400.01 ±0.53	1411.84 ±0.52	−18.73 ±0.51	−6.90 ±0.50
1,2-Dimethyl-3-ethylbenzene	$C_{10}H_{14}$	1398.90 ±0.62	1411.63 ±0.61	−19.84 ±0.61	−7.11 ±0.60
1,2-Dimethyl-4-ethylbenzene	$C_{10}H_{14}$	1398.36 ±0.62	1410.83 ±0.61	−20.38 ±0.61	−7.91 ±0.60
1,3-Dimethyl-2-ethylbenzene	$C_{10}H_{14}$	1398.90 ±0.62	1411.63 ±0.61	−19.84 ±0.61	−7.11 ±0.60
1,3-Dimethyl-4-ethylbenzene	$C_{10}H_{14}$	1398.36 ±0.62	1410.83 ±0.61	−20.38 ±0.61	−7.91 ±0.60
1,3-Dimethyl-5-ethylbenzene	$C_{10}H_{14}$	1397.88 ±0.62	1410.24 ±0.61	−20.86 ±0.61	−8.50 ±0.60
1,4-Dimethyl-2-ethylbenzene	$C_{10}H_{14}$	1398.36 ±0.62	1410.83 ±0.61	−20.38 ±0.61	−7.91 ±0.60
1,2,3,4-Tetramethylbenzene	$C_{10}H_{14}$	1395.70 ±0.72	1408.72 ±0.71	−23.04 ±0.71	−10.02 ±0.70
1,2,3,5-Tetramethylbenzene	$C_{10}H_{14}$	1395.20 ±0.72	1408.03 ±0.71	−23.54 ±0.71	−10.71 ±0.70
1,2,4,5-Tetramethylbenzene	$C_{10}H_{14}$	1395.16 ±0.72	1407.92 ±0.71	−23.58 ±0.71	−10.82 ±0.70
n-Amylbenzene	$C_{11}H_{16}$		1572.88 ±0.34		−8.23 ±0.37
n-Hexylbenzene	$C_{12}H_{18}$		1730.33 ±0.36		−13.15 ±0.39
n-Heptylbenzene	$C_{13}H_{20}$		1887.77 ±0.39		−18.08 ±0.42
n-Octylbenzene	$C_{14}H_{22}$		2045.21 ±0.42		−23.00 ±0.46
n-Nonylbenzene	$C_{15}H_{24}$		2202.66 ±0.46		−27.93 ±0.50
n-Decylbenzene	$C_{16}H_{26}$		2360.10 ±0.50		−32.86 ±0.54
n-Undecylbenzene	$C_{17}H_{28}$		2517.54 ±0.55		−37.78 ±0.59
n-Dodecylbenzene	$C_{18}H_{30}$		2674.98 ±0.59		−42.71 ±0.64
n-Tridecylbenzene	$C_{19}H_{32}$		2832.43 ±0.64		−47.63 ±0.69
n-Tetradecylbenzene	$C_{20}H_{34}$		2989.87 ±0.70		−52.56 ±0.75
n-Pendadecylbenzene	$C_{21}H_{36}$		3147.31 ±0.75		−57.49 ±0.80
n-Hexadecylbenzene	$C_{22}H_{38}$		3304.76 ±0.80		−62.41 ±0.85
Δ per CH_2	CH_2		157.443		−4.926

[a] $-\Delta Hc°$ represents the heat evolved in the combustion of the given hydrocarbon, in gaseous oxygen to form gaseous carbon dioxide and liquid water, at 25° C and constant pressure, with all reactants and products in their appropriate standard reference states.

[b] $\Delta Hf°$ represents the increment in the heat content or enthalpy of the process of forming the given hydrocarbon in the state indicated, from its elements, at 25° C, with all reactants and products in their appropriate standard reference states.

TABLE 2.—*Comparison of previous experimental data with the selected "best" values from this report for the heats of combustion of the alkylbenzenes.*

Compound	Investigators	Year	Reference	Heat of combustion	
				Difference from value of this report [a]	Estimated uncertainty of the difference [b]
				kcal/mole	*kcal/mole*
Benzene (liquid)	Berthelot	1878	[12]	−3.8	±3.9
	Stohmann, Rodatz, and Herzberg.	1886	[15]	0.0	±1.6
	Stohmann, Kleber, and Langbein.	1889	[16]	−0.6	±1.6
	Richards, Henderson and Frevert.	1907	[17]	−2.5	±1.6
	Richards and Jesse	1910	[18]	+1.5	±1.6
	Roth and von Auwers	1915	[19]	+2.1	±1.6
	Richards and Barry	1915	[20]	−0.2	±1.6
	Richards and Davis	1920	[21]	+1.9	±1.6
Benzene (gas)	Berthelot	1881	[13]	−3.2	±3.9
	Thomsen	1886	[14]	−11.4	±7.9
	Stohmann, Rodatz, and Herzberg.	1886	[15]	−0.4	±1.6
	Stohmann, Rodatz, and Herzberg.	1887	[22]	+0.8	±1.9
Toluene (liquid)	Schmidlin	1906	[23]	+5.6	±4.7
	Roth and von Auwers	1915	[19]	+1.6	±1.9
	Richards and Barry	1915	[20]	+2.7	±1.9
	Richards and Davis	1917	[24]	+2.5	±1.9
	Richards and Davis	1920	[21]	+2.0	±1.9
Ethylbenzene (liquid)	Jesse	1912	[25]	−10.8	±2.2
	Moureu and André	1914	[26]	+5.8	±3.3
	Richards and Barry	1915	[20]	+0.2	±2.2
	von Auwers and Kolligs	1922	[27]	+4.3	±2.2
o-Xylene (liquid)	Stohmann, Rodatz, and Herzberg.	1887	[22]	−2.1	±2.2
	Richards and Barry	1910	[20]	+3.5	±2.2
m-Xylene (liquid)	Stohmann, Rodatz, and Herzberg.	1887	[22]	−2.0	±2.2
	Richards and Jesse	1910	[18]	+3.7	±2.2
	Roth and von Auwers	1915	[19]	+2.5	±2.2
p-Xylene (liquid)	Stohmann, Rodatz, and Herzberg.	1887	[22]	−2.1	±2.2
	Richards and Jesse	1910	[18]	−2.1	±2.2
n-Propylbenzene	Genvresse	1893	[28]	+3.9	±3.7
	Richards and Barry	1915	[20]	−0.7	±2.5
	Huffman and Knowlton	1944	[29]	−1.0	±0.6
Isopropylbenzene (liquid)	Genvresse	1893	[28]	+6.2	±3.7
	Richards and Barry	1915	[20]	+0.9	±2.5
	Huffman and Knowlton	1944	[29]	−1.2	±0.6
1,2,4-Trimethylbenzene (liquid)	Richards and Barry	1915	[20]	−0.9	±2.5
1,3,5-Trimethylbenzene (liquid)	Stohmann, Rodatz, and Herzberg.	1887	[22]	+11.8	±2.5
	Richards and Barry	1915	[20]	+2.4	±2.5
tert-Buthylbenzene	Richards and Barry	1915	[20]	−1.4	±2.8
	Richards and Davis	1920	[21]	+0.1	±2.8
1-Methyl-3-n-propylbenzene (liquid).	Genvresse	1893	[28]	+7.5	±4.2
1-Methyl-3-isopropylbenzene (liquid).	....do	1893	[28]	+12.4	±4.2
1-Methyl-4-isopropylbenzene (liquid).	Stohmann, Rodatz, and Herzberg.	1887	[22]	+4.0	±2.8
	Stohmann, Kleber, and Langbein.	1890	[30]	+15.0	±2.8
1,2,4,5-Tetramethylbenzene (liquid).	Stohmann, Kleber, and Langbein.	1889	[16]	+1.2	±2.8

[a] Insofar as significant, the previous value was converted to the present unit of energy and atomic weights. A negative sign in this column indicates that the earlier value is less than that of the present report; a positive sign, higher.

[b] The uncertainties have been assigned by the present authors.

VII. REFERENCES

[1] E. F. Mueller and F. D. Rossini. Am. J. Physics **12,** 1 (1944).
[2] G. P. Baxter, M. Guichard, O. Hönigschmid, and R. Whytlaw-Gray. J. Am. Chem. Soc. **63,** 845 (1941).
[3] F. D. Rossini and W. E. Deming. J. Wash. Acad. Sci. **29,** 416 (1939).
[4] E. J. Prosen, R. S. Jessup, and F. D. Rossini. J. Research NBS **33,** 447 (1944) RP1620.
[5] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini. J. Research NBS **34,** 143 (1945) RP1634.
[6] E. J. Prosen, R. Gilmont, and F. D. Rossini. J. Research NBS **34,** 65 (1945) RP1629.
[7] W. H. Johnson, E. J. Prosen, and F. D. Rossini. J. Research NBS **35,** 141 (1945) RP1665.
[8] W. H. Johnson, E. J. Prosen, and F. D. Rossini. National Bureau of Standards. Unpublished data.
[9] D. D. Wagman, W. J. Taylor, J. Pignocco, and F. D. Rossini. National Bureau of Standards. Unpublished data.
[10] N. C. Osborne and D. C. Ginnings. National Bureau of Standards. Unpublished data.
[11] E. J. Prosen and F. D. Rossini. J. Research NBS **34,** 263 (1945) RP1642.
[12] M. Berthelot, Ann. chim. [5] **13,** 1 (1878).
[13] M. Berthelot, Ann chim. phys. [5] **23,** 193 (1881).
[14] J. Thomsen, Thermochemische Untersuchungen, **4,** J. A. Barth, Leipzig, (1886).
[15] F. Stohmann, P. Rodatz, and H. Herzberg, J. prakt. Chem. **33,** 241 (1886).
[16] F. Stohmann, C. Kleber, and H. Langbein, J. prakt. Chem. **40,** 77 (1889).
[17] T. W. Richards, L. J. Henderson, and H. L. Frevert, Proc. Am. Acad. **42,** 573 (1907); *Z.* physik. Chem. **59,** 532 (1907).
[18] T. W. Richards and R. H. Jesse, Jr., J. Am. Chem. Soc. **32,** 268 (1910).
[19] W. A. Roth and K. von Auwers, Liebigs Ann. Chem. **407,** 145 (1915).
[20] T. W. Richards and F. Barry, J. Am. Chem. Soc. **37,** 993 (1915).
[21] T. W. Richards and H. S. Davis, J. Am. Chem. Soc. **42,** 1599 (1920).
[22] F. Stohmann, P. Rodatz, and W. Herzberg, J. prakt. Chem. **35,** 22 (1887).
[23] Schmidlin, Ann. chim. phys. [8] **7,** 245 (1906).
[24] T. W. Richards and H. S. Davis, J. Am. Chem. Soc. **39,** 341 (1917).
[25] R. H. Jesse, Jr., J. Am. Chem. Soc. **34,** 1337 (1912).
[26] C. Moureu and E André, Ann chim. **1,** 113 (1914).
[27] K. von Auwers and H. Kolligs, Ber. Chem. Ges. **55,** 3872 (1922).
[28] P. Genvresse, Bul. soc. chim **9,** 219 (1893).
[29] H. M. Huffman and J. W. Knowlton, private communication (1944).
[30] F. Stohmann, C. Kleber, and H. Langbein, *Z.* phys. Chem. **6,** 338 (1890)

WASHINGTON, December 11, 1945.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1715

Part of Journal of Research of the National Bureau of Standards, Volume 36, May 1946

HEATS OF COMBUSTION OF FOUR CYCLOPENTANE AND FIVE CYCLOHEXANE HYDROCARBONS

By Walter H. Johnson, Edward J. Prosen, and Frederick D. Rossini

ABSTRACT

The heats of combustion of cyclopentane, methylcyclopentane, ethylcyclopentane, *n*-propylcyclopentane, cyclohexane, methylcyclohexane, ethylcyclohexane, *n*-propylcyclohexane, and *n*-butylcyclohexane were measured with a bomb calorimeter. The following values were obtained for $-\Delta Hc°_{298.16}$, the heat of combustion at 25° C and constant pressure of the liquid hydrocarbon in gaseous oxygen to form gaseous carbon dioxide and liquid water, with all the reactants and products in their thermodynamic standard reference states, in international kilojoules per mole (with the corresponding value in terms of the conventional thermochemical calorie being given in parentheses):

Cyclopentane, 3290.34 ±0.72 (786.54 ±0.17)
Methylcyclopentane, 3937.07 ±0.75 (941.14 ±0.18)
Ethylcyclopentane, 4591.17 ±0.94 (1097.50 ±0.22)
n-Propylcyclopentane, 5244.75 ±1.18 (1253.74 ±0.28)
Cyclohexane, 3919.26 ±0.70 (936.88 ±0.17)
Methylcyclohexane, 4564.52 ±0.95 (1091.13 ±0.23)
Ethylcyclohexane, 5221.71 ±1.46 (1248.23 ±0.35)
n-Propylcyclohexane, 5874.79 ±1.15 (1404.34 ±0.27)
n-Butylcyclohexane, 6529.21 ±1.22 (1560.78 ±0.29).

CONTENTS

		Page
I.	Introduction	463
II.	Units and constants	464
III.	Method, apparatus, and procedure	464
IV.	Materials	464
V.	Results	465
VI.	References	468

I. INTRODUCTION

In continuation of the program of the Bureau's thermochemical laboratory of determining the heats of combustion, formation, and isomerization of hydrocarbons of various types, calorimetric measurements have been made of the heats of combustion of nine cycloparaffin hydrocarbons, including the first four members of the normal alkylcyclopentane series and the first five members of the normal alkycyclohexane series. This report gives the details of the experimental work and results.

II. UNITS AND CONSTANTS

The unit of energy upon which the experimental values of this investigation are based is the international joule determined by the standards of resistance (international ohms), electromotive force (international volts), and time (mean solar seconds) maintained at this Bureau.

The following relation was used to convert the values to the conventional thermochemical calorie [1][1]:

4.1833 international joules=1 calorie.

The molecular weight of carbon dioxide, the mass of which was used to determine the amount of reaction, was taken as 44.010 from the 1941 table of International Atomic Weights [2].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [3]. In other cases, reasonable estimates of the uncertainty were made.

Definitions of the symbols used are given in previous papers [4, 5, 6, 7, 8].

III. METHOD, APPARATUS, AND PROCEDURE

The method and apparatus used in this investigation are described in previous papers [4, 5, 6, 7, 8]. Calorimeter system *F* was used in the experiments on all the compounds of the present work except those on *n*-butylcyclohexane. Calorimeter system *D*, described in reference [6], was used in these latter experiments. Calorimeter system *F* differed from system *D* in that a new bomb and heater, made of the same design as those of system *D*, were used. Resistance bridge No. 404 and platinum resistance thermometer No. 373,730 were used for all the experiments reported here.

The method of sealing the samples of hydrocarbons in glass ampoules, the ignition of the hydrocarbons in the bomb, the purification of the oxygen used for combustion, the examination of the products of combustion, and the determination of the amount of reaction were the same as previously described [4, 5 6]. No products of incomplete combustion were found in any of the experiments.

The procedure used in the combustion experiments and the method of determining the ignition energy and of correcting for the formation of nitric acid were the same as previously described [4, 5, 6].

IV. MATERIALS

The samples of API–NBS hydrocarbons have been made available by the American Petroleum Institute and the National Bureau of Standards through the API Research Project 44 on the "Collection, analysis, and calculation of data on the properties of hydrocarbons." The samples were purified by the API Research Project 6 on the "Analysis, purification, and properties of hydrocarbons," from material supplied by the following laboratories:

[1] Figures in brackets indicate the literature references at the end of this paper.

Cyclopentane, ethylcyclopentane, *n*-propylcyclopentane, ethylcyclohexane, *n*-propylcyclohexane, *n*-butylcyclohexane, and half of the methylcyclohexane, by the API Research Project 45 on the "Synthesis and properties of hydrocarbons of low molecular weight" at the Ohio State University, under the supervision of Cecil E. Boord.

Cyclohexane, and half of the methylcyclohexane, by the Barrett Division of the Allied Chemical & Dye Corporation.

Methylcyclopentane, by the Houdry Process Corporation, through the courtesy of E. A. Smith.

A complete description of the purification and determination of purity of these compounds are given in other reports [10, 11]. The mole fractions of impurity in these samples, as determined by A. R. Glasgow, Jr., E. T. Murphy, and A. J. Streiff from time-temperature freezing and melting curves and as described in reference [12], were as follows: Cyclopentane, 0.0002 ± 0.0001; methylcyclopentane, 0.0016 ± 0.0006; ethylcyclopentane, 0.0008 ± 0.0003; *n*-propylcyclopentane, 0.0019 ± 0.0010; cyclohexane, 0.00003 ± 0.00002; methylcyclohexane, 0.0010 ± 0.0008; ethylcyclohexane, 0.0011 ± 0.00008; *n*-propylcyclohexane, <0.003 (preliminary value); *n*-butylcyclohexane <0.003 (preliminary value) [10, 11].

As the manner of purification of these compounds [10, 11] was such as to leave substantially only close-boiling isomeric impurities in the respective compounds, it is calculated that in the worst case the measured heat of combustion would be affected by less than 0.005 percent because of impurities in the compound.

V. RESULTS

The energy equivalents of calorimeter systems *C* and *D* are (see section VI–1 of reference [6]):

$$E_s(C) = 137717.4 \pm 13.9 \text{ int. j/ohm.}$$
$$E_s(D) = 136489.6 \pm 14.5 \text{ int. j/ohm.}$$

The results of the experiments to determine the energy equivalent of calorimeter system *F*, through its ratio to that of calorimeter system *C* by the combustion of benzoic acid, are given in table 1. The symbols at the heads of the columns are as defined in references [4, 5, 6]. The energy equivalent of calorimeter system *F*, together with its estimated over-all uncertainty, is

$$E_s(F) = 0.992496\ E_s(C)$$
$$= 136684.0 \pm 19.0 \text{ int. j/ohm.}$$

For convenience and clarity the data are all reported in terms of the energy equivalent of calorimeter system *F*.

The results of the combustion experiments on cyclopentane, methylcyclopentane, ethylcyclopentane, *n*-propylcyclopentane, cyclohexane, methylcyclohexane, ethylcyclohexane, *n*-propylcyclohexane, and *n*-butylcyclohexane are given in table 2. The symbols at the heads of the columns are as defined in references [4, 5, 6]. The value of *B* for *n*-butylcyclohexane is given in terms of calorimeter system *F*, with the ratio of $E_s(F)$ to $E_s(D)$.

TABLE 1.—*Energy equivalent calorimeter system F*

Experiment number	Mass of benzoic acid[a]	k	K	U	ΔR_c	Δr_i	Δr_n	B'	Deviation from mean
	g	*min*$^{-1}$	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm/g of benzoic acid*	*Ohm/g of benzoic acid*
1	1.51711	0.001985	0.001082	0.000296	0.293732	0.000410	0.000005	0.1933711	0.0000317
2	1.51864	.001979	.001140	.000280	.293998	.000418	.000007	.1933434	−.0000040
3	1.52204	.001976	.001194	.000338	.293638	.000413	.000005	.1933385	−.0000089
4	1.51768	.001965	.001190	.000355	.293768	.000420	.000005	.1933141	−.0000253
5	1.51642	.001963	.000998	.000379	.293537	.000412	.000004	.1933290	−.0000095
Mean								0.1933394	
Standard deviation of the mean								±.0000094	

[a] NBS Standard Sample 39f.

TABLE 2.—*Results of the calorimetric combustion experiments*

Compound (liquid)	Number of experiments	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B	
									Mean	Standard deviation of mean
Cyclopentane	5	2.65418 to 2.70407	0.001973 to .001981	0.001141 to .001268	0.000248 to .000333	0.290298 to .295049	0.000418 to .000430	0.000011 to .000012	0.1091973	±0.0000075
Methylcyclopentane	6	2.69351 to 2.75965	.001972 to .001992	.000946 to .001200	.000251 to .000331	.293636 to .300909	.000423 to .000429	.000011 to .000012	.1088636	±.0000045
Ethylcyclopentane	6	2.68285 to 3.00924	.001965 to .001987	.000819 to .001248	.000245 to .000334	.292316 to .327896	.000419 to .000427	.000010 to .000013	.1088346	±.0000062
n-Propylcyclopentane	7	2.67656 to 2.76082	.001970 to .001980	.001006 to .001314	.000213 to .000362	.291493 to .300782	.000417 to .000427	.000010 to .000011	.1087869	±.0000080
Cyclohexane	6	2.50354 to 2.77753	.001964 to .001974	.000915 to .001763	.000270 to .000346	.271925 to .301417	.000410 to .000431	.000006 to .000009	.1083894	±.0000029
Methylcyclohexane	6	2.50695 to 2.99699	.001965 to .001972	.000251 to .001746	.000290 to .000413	.271685 to .324614	.000411 to .000430	.000009 to .000012	.1082005	±.0000064
Ethylcyclohexane	5	1.68309 to 2.68037	.001955 to .001986	.001236 to .004197	.000214 to .000422	.182730 to .290810	.000413 to .000427	.000008 to .000010	.1083063	±.0000121
n-Propylcyclohexane	6	2.61019 to 2.75202	.001968 to .001976	.001047 to .001425	.000301 to .000368	.283102 to .298494	.000419 to .000429	.000007 to .000009	.1083144	±.0000052
n-Butylcyclohexane	6	2.63440 to 2.77833	.001982 to .002005	.001013 to .001432	.000243 to .000333	.286302 to .301826	.000407 to .000417	.000037 to .000040	.1083424	±.0000064

[a] This value has been converted to apply to calorimeter system F (see text).

In table 3 are given the final results for the four cyclopentane and five cyclohexane hydrocarbons whose heats of combustion were measured in the present investigation. The columns give the value of B for 28° C, in ohms per gram of carbon dioxide, as given in table 2; B°, which is B corrected to the ideal bomb reaction [8]; $-\Delta U^\circ$, the decrement in internal energy for the ideal reaction of combustion at 28° C, with all reactants and products in their thermodynamic standard reference states of unit fugacity, in international kilojoules per mole of hydrocarbon; $-\Delta Hc^\circ$, the decrement in heat content or enthalpy (or heat evolved in the combustion at constant pressure) for the reaction of combustion of the liquid hydrocarbon at 28° C, with all the reactants and products in their thermodynamic standard reference states; and finally, the same quantity, $-\Delta Hc^\circ$, for the reaction of combustion at 25° C. The foregoing values of $-\Delta U^\circ$ and $-\Delta Hc^\circ$ apply to the reaction.

$$C_aH_b(\text{liq})+\left(a+\frac{b}{4}\right)O_2(g)=aCO_2(g)+\frac{b}{2}H_2O(\text{liq}).$$

TABLE 3.—*Values of the heats of combustion*

Compound (liquid)	B at 28° C	B° at 28° C	$-\Delta U^\circ$ at 28° C
	Ohm/g CO_2	*Ohm/g* CO_2	*Int. kj/mole*
Cyclopentane	0.1091973 ±0.0000150	0.1091668 ±0.0000150	3283.44 ±0.72
Methylcyclopentane	.1088836 ±0.0000090	.1088531 ±0.0000090	3928.81 ±0.75
Ethylcyclopentane	.1088346 ±0.0000124	.1088039 ±0.0000124	4581.54 ±0.94
n-Propylcyclopentane	.1087869 ±0.0000160	.1087564 ±0.0000160	5233.76 ±1.18
Cyclohexane	.1083894 ±0.0000058	.1083590 ±0.0000060	3910.98 ±0.70
Methylcyclohexane	.1082005 ±0.0000128	.1081707 ±0.0000128	4554.88 ±0.95
Ethylcyclohexane	.1083063 ±0.0000242	.1082772 ±0.0000240	5210.70 ±1.46
n-Propylcyclohexane	.1083144 ±0.0000104	.1082841 ±0.0000104	5862.41 ±1.15
n-Butylcyclohexane	.1083424 ±0.0000128	.1083121 ±0.0000128	6515.47 ±1.22

Compound (liquid)	$-\Delta Hc^\circ$ (liq) at 28° C	$-\Delta Hc^\circ$ (liq) at 25° C	
	Int. kj/mole	*Int. kj/mole*	*kcal/mole*
Cyclopentane	3289.70 ±0.72	3290.34 ±0.72	786.54 ±0.17
Methylcyclopentane	3936.32 ±0.75	3937.07 ±0.75	941.14 ±0.18
Ethylcyclopentane	4590.30 ±0.94	4591.17 ±0.94	1097.50 ±0.22
n-Propylcyclopentane	5243.77 ±1.18	5244.75 ±1.18	1253.74 ±0.28
Cyclohexane	3918.49 ±0.70	3919.26 ±0.70	936.88 ±0.17
Methylcyclohexane	4563.64 ±0.95	4564.52 ±0.95	1091.13 ±0.23
Ethylcyclohexane	5220.71 ±1.46	5221.71 ±1.46	1248.23 ±0.35
nPropycyclohexane	5873.68 ±1.15	5874.70 ±1.15	1404.34 ±0.27
n-Butylcyclohexane	6527.99 ±1.22	6529.21 ±1.22	1560.78 ±0.29

The over-all uncertainty assigned to each final value of the heat of combustion of a given compound was taken as the square root of the sum of the squares of the following: (a) Twice the standard deviation of the mean of the series of combustion experiments, (b) an uncertainty of 0.010 percent in the determination of the absolute value of the amount of reaction, (c) twice the standard deviation of the mean of the series of experiments for determining the energy equivalent of the calorimeter with electric energy and of the series of experiments to determine the ratios of the energy equivalents, and (d) an uncertainty of 0.010 percent in the determination of the absolute value of the energy equivalent, with electric energy.

n-Butylcyclohexane. * This value has been converted to apply to calorimeter system A' (see text).

Following the usual practice of the Bureau's Thermochemical Laboratory, the values reported in this investigation are being utilized in the calculation of the heats of formation for the same compounds, in the gaseous as well as the liquid state, and in the evaluation by the method of increments per CH_2 group [9] of the values of the heats of combustion and formation for the higher normal alkylcyclopentanes and normal alkylcyclohexanes.

VI. REFERENCES

[1] E. F. Mueller and F. D. Rossini, Am. J. Physics **12,** 1 (1944).
[2] G. P. Baxter, M. Guichard, O. Hönigschmid, and R. Whytlaw-Gray, J. Am. Chem. Soc. **63,** 845 (1941).
[3] F. D. Rossini and W. E. Deming, J. Wash. Acad. Sci. **29,** 416 (1939).
[4] E. J. Prosen and F. D. Rossini, J. Research NBS **27,** 289 (1941) RP1420.
[5] E. J. Prosen and F. D. Rossini, J. Research NBS **33,** 255 (1944) RP1607.
[6] E. J. Prosen and F. D. Rossini, J. Research NBS **33,** 439 (1944) RP1619.
[7] E. J. Prosen, R. Gilmont, and F. D. Rossini, J. Research NBS **34,** 65 (1945) RP1629.
[8] W. H. Johnson, E. J. Prosen, and F. D. Rossini, J. Research NBS **35,** 141 (1945) RP1665.
[9] E. J. Prosen and F. D. Rossini. J. Research NBS **34,** 263 (1945) RP1642.
[10] A. R. Glasgow, Jr., E. T. Murphy, C. B. Willingham, and F. D. Rossini, National Bureau of Standards, API Research Project 6. Unpublished.
[11] A. J. Streiff, E. T. Murphy, C. B. Willingham, V. A. Sedlak, and F. D. Rossini. National Bureau of Standards, API Research Project 6. Unpublished.
[12] A. R. Glasgow, Jr., A. J. Streiff, and F. D. Rossini, J. Research NBS **35,** 355 (1945) RP1676.

WASHINGTON, December 11, 1945.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1716

Part of Journal of Research of the National Bureau of Standards, Volume 36, May 1946

SIZE GRADING OF DIAMOND POWDER

By B. L. Steierman, H. Insley, and W. H. Parsons

ABSTRACT

A study has been carried out on certain aspects of diamond-powder grading. Various liquids were tried as dispersing media, and of the 30 materials tested, gelatin solution was found to be the best. Several methods of separating the powder into size fractions were investigated and are discussed. The Cooke short-column elutriator was found satisfactory for determining the size of large quantities of powder with little manual attention. Results of size fractionation are shown by photomicrographs.

CONTENTS

	Page
I. Introduction	469
II. Dispersing media	469
III. Methods of size separation	471
1. Sieving	471
2. Sedimentation	472
(a) Direct settling	473
(b) Elutriation	474
IV. Discussion	476
V. Commercial standard and specification	477
VI. Summary	478

I. INTRODUCTION

Before 1940 the diamond dies for wire drawing used in this country were made abroad. After the manufacture of diamond dies was begun in this country, it became evident that the domestic supply of diamond powder used for drilling these dies was not of proper quality. The present project was undertaken with three general aims: first, to determine the efficiency of various methods for separating diamond powder into size fractions; second, to determine the best dispersants for diamond powder; and third, to obtain data suitable for a basis for writing a standard covering the size and grading of diamond powder for commercial producers and users. It is also believed that the results may be of use in the sizing and grading of powders other than diamond.

II. DISPENSING MEDIA

For any method of sedimenting, elutriating, or examining diamond powder in a liquid, a suitable dispersing agent is necessary. In order

to be effective as a dispersant, a liquid must be able to wet diamond and to develop an electric charge on the particles. If the liquid does not wet the diamond particles, agglomeration will not be overcome, because of surface tension of the liquid. Furthermore, it is apparent that if the particles are neutral electrically, there will be no repulsive effect between particles. However, particles having like charges will repel each other, and hence will not tend to aggregate.

The wetting power of a liquid with respect to diamond was determined by mixing a small quantity of liquid and diamond powder on a glass slide. If the liquid flowed over the powder and enveloped it, that particular liquid was judged to wet diamond. On the other hand, if the liquid pushed the powder away it did not wet diamond.

A small electrophoresis cell was used for determining the kind of charge developed on diamond when in contact with a liquid. This cell was a glass microscope slide with two aluminum electrodes cemented to it about 1 mm apart. A drop of liquid with added diamond powder was placed on the slide and covered with a cover glass. Leads from a 110-volt direct-current line were connected to the electrodes. The cell was placed under a microscope, and the movement of the particles was observed. If the particles moved toward the positive electrode, the charge of the particle was negative. Diamond developed a negative electric charge in contact with all the liquids tried.

The method used in determining the degree of dispersion was examination by dark and bright field illumination. The liquid to be tested was mixed with a small quantity of fine (approximately 1 micron) diamond powder in a vial or on a microscope slide and then examined microscopically. The presence or absence of aggregates, separation of the particles, and Brownian movement were observed, and a rating of excellent, good, fair, or poor was given. Due regard was taken of the effect of viscosity on the Brownian movement. Table 1 shows the relation of the rating to the appearance of the powder under the microscope. The results of the dispersing tests are given in table 2.

TABLE 1.—*Relation of rating to appearance of the powder under the microscope*

Rating	Aggregates	Brownian movement
Excellent	Few or none	Violent except for very viscous liquid.
Good	Few, small (10 to 20 microns)	Particles quite active.
Fair	Abundant, small to medium (30 to 50 microns).	Some activity.
Poor	Large aggregates	Practically none.

After testing the liquids (see table 2), the solution of gelatin in water was selected as best suited for a suspending medium for sedimentation. This solution contains between 0.1 and 0.25 percent of gelatin, with sodium carbonate added to give a pH of 9. A few drops of thymol were added to prevent the growth of fungi or bacteria. The gelatin solution besides giving good dispersion has the added advantage of a viscosity approximately as low as water. This results in giving sedimentation velocities that are relatively high, much higher than if more viscous liquids, such as pine or olive oil, were

used. Comparison with pine oil, alcohol, ethylene glycol, and other liquids indicates that the gelatin solution is also the cheapest and most easily procured dispersant.

TABLE 2.—*Dispersive power of liquids*

Liquid	Dispersive power	Remarks
Triethanolamine	Fair	No Brownian movement; viscous, toxic, expensive.
Heraldehyde	Good	Too volatile.
Flexol	Poor	Extreme aggregation.
Kapsol (methoxyethyloleate)	do	
Butoxy ethyl stearate	Fair	Expensive.
Methylcellosolve	do	Very viscous.
Glycol sebacate	Good	Do.
Machine oil	Poor	
Transformer oil	Fair	
Octoil	do	
Ethyl alcohol	Poor	Too volatile, bad aggregation.
1-percent calgon in water	do	Does not wet diamond.
Kerosine	Fair	
1 percent oleic acid in kerosine	do	
Oleic acid	Good	Viscous and expensive.
Olive oil	do	Too viscous.
Ethylene glycol	do	
Mineral oil	Fair	Do.
Castor oil	do	Do.
Glycerine	Poor	
1 percent aerosol in water	do	
Pine oils	Good, excellent	Series of oils in various viscosities.
0.1 to 0.25 percent gelatin solution in water.	Excellent	Na_2CO_3 to give pH of 9. Thymol as germicide.
Diamond drill oil	Good	Too viscous.
Bayol	Poor	
Fractol A	do	
0.2 percent calcium lignin sulfonate in water.	Good	
Canada balsam	Excellent	Viscous, used for photomicrographs.
Hyrax	do	Solid at room temperature.

III. METHODS OF SIZE SEPARATION

1. SIEVING

Only a comparatively small amount of time was devoted to a study of sieving because the subject has been treated at length in the literature on grinding, milling, and particle-size analysis and also because the present investigation was mainly concerned with diamond powder of subsieve sizes.

The diamond crystals were crushed in a diamond mortar and sieved dry. Four sieves (diameter 3 inches) were used in a stacked arrangement—U. S. Standard Sieve Nos. 170, 200, 275, and 325. The sieving was done by hand, combining rotary and sidewise shaking with tapping, perpendicular to the sieve.

Microscopic examination of the sieved fraction showed considerable amounts of very fine particles to be present. These particles adhered to the surfaces of the larger grains. In order to remove these fine particles, the powder retained on a No. 325 sieve was poured into a beaker of acetone, stirred vigorously, quickly sedimented, and the fines still in suspension were poured off. This process was repeated several times. Then the sedimented powder was washed with acetone and dried. The supernatant acetone containing the fines was evaporated, and the fine particles were added to the less than

No. 325 sieve fraction. Sieving, as here described, gave very uniform results. The particle-size range was narrow. Micrographs of two fractions are shown in figures 1 and 2.

2. SEDIMENTATION

In order to use any settling method it is necessary to calculate a table of settling velocities. The calculations are based on Stokes' law:

$$V=(2/9)ga^2(D_1-D_2)1/\eta,$$

where

V=sedimentation velocity, cm/sec
g=980 cm/sec^2
a=radius of particles
D_1=density of diamond, 3.52
D_2=density of gelatin solution, 0.99
η=coefficient of viscosity, poises.

This equation can be simplified as follows:

$$V=a^2K,$$

where

$K=551\theta$
θ=fluidity of gelatin solution, $1/\eta$
$V=(2/9)980(3.52-.99)a^2 1/\eta$
$V=551a^2\theta$.

Table 3 gives the values of K and θ for various temperatures, based on the use of gelatin solution, also a table of diameters and radii of particles. Table 4 gives the sedimentation rates for diamonds of various sizes and grades.

TABLE 3.—*Factors used to determine settling rates of diamond powder in gelatin solution*

T	K	θ
°C		
15	48,300	87.69
17.5	51,335	93.53
20.0	54,800	99.50
22.5	58,220	105.63
23.0	58,890	106.86
25	61,610	111.91

DIAMETERS AND RADII OF PARTICLES			
Diameter	Radius	a	a^2
Microns	*cm*	$cm\times10^{-4}$	$cm\times10^{-8}$
2	0.00010	10	100
5	.00025	25	625
8	.00040	40	1,600
10	.00050	50	2,500
15	.00075	75	5,625
25	.00125	125	15,625
35	.00175	175	30,625
55	.00275	275	75,625
70	.00350	350	122,500
85	.00425	425	180,625
120	.00600	600	360,000

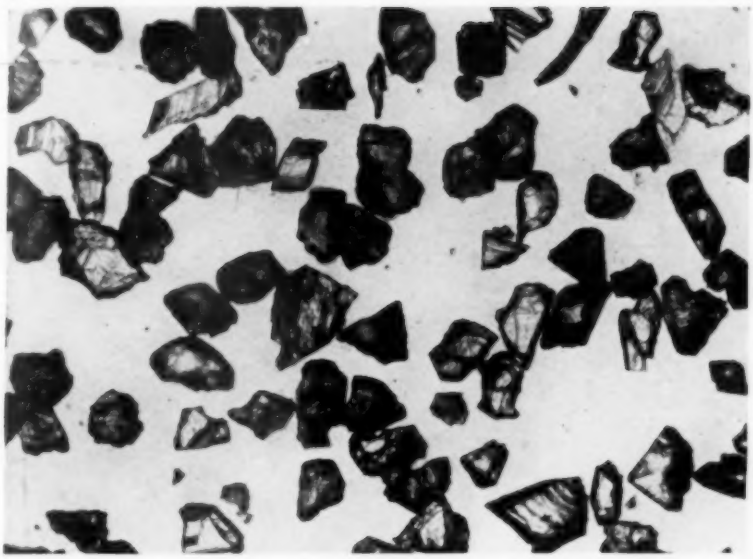

FIGURE 1.—*Sieved fraction of diamond powder through No. 200 sieve and retained on No. 270.*

Magnification, × 200.

FIGURE 2.—*Sieved fraction of diamond powder through No. 270 sieve and retained on No. 325.*

Magnification, × 200.

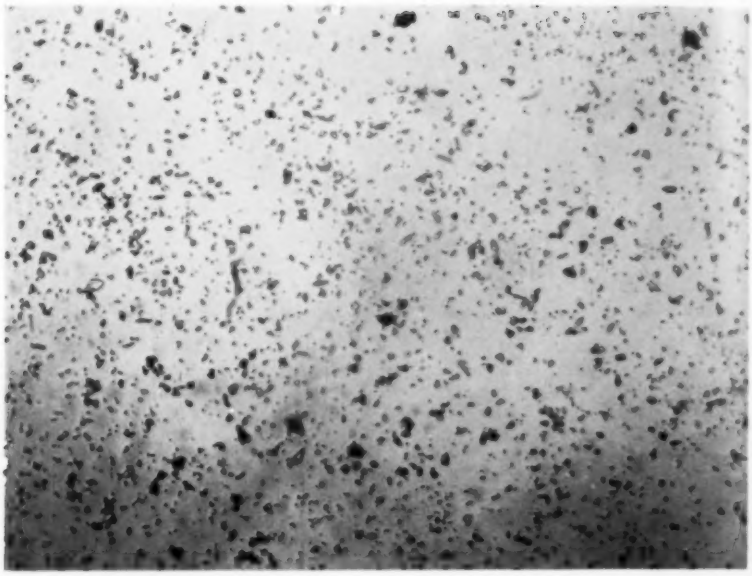

FIGURE 3.—*Diamond powder fraction by settling, average size 1.5 microns.*
Magnification, × 400.

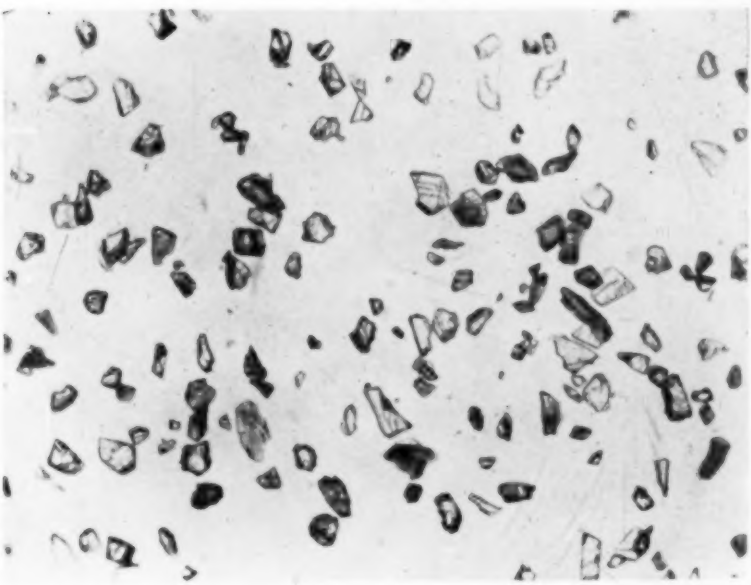

FIGURE 4.—*Diamond powder fraction by settling, average size 7 microns.*
Magnification, × 400.

TABLE 4.—*Sedimentation rates for diamond in gelatin solution*

[Temperature, 25° C, when $V=a^2 61{,}610$]

Grade designation	Maximum size of diamond particle	a^2	V	$1/V$	$5/V$	Time required to settle 5 cm		
	Microns	$cm \times 10^{-10}$	*cm/sec*	*sec/cm*	*sec/5 cm*	*hr*	*min*	*sec*
1	2	100	0.0006	1,666	8,330	2	18	50
3	5	625	.0039	256	1,280		21	20
5	8	1,600	.0099	101	505		8	25
7	10	2,500	.0154	64.9	324		5	25
9	20	10,000	.0616	16.2	81		1	21
12	37	34,225	.2107	4.7	24			24
20	60	90,000	.5545	1.8	9			9
40	85	180,625	1.114		5			5
60	120	360,000	2.220		2			2

(a) DIRECT SETTLING

Some tests were performed to determine the efficiency of direct settling as a method of size separation of diamond powder. The diamond powder was mixed with a small quantity of the gelatin solution prepared as mentioned in section II and stirred for one-half hour with an electric mixer. The suspension was diluted to a volume of 2 liters and placed in an asbestos-jacketed enamel can about 12 cm in diameter. The asbestos lagging was used to prevent radiation losses and to reduce convection currents.

After the stirring, the suspension was allowed to settle for a length of time such that all particles greater in size than the finest desired fraction had settled 5 cm. The upper liquid was then drawn off. A rack was constructed so that it could be used to set a pipette to remove liquid to a predetermined depth. The tip of the pipette was bent at right angles to its length so as not to withdraw material that had settled below the desired depth. This sedimentation was repeated several times, each time making the suspension up to the original volume, and again stirring and settling before removing a fraction. The withdrawals were all combined as the finest fraction and concentrated by centrifuging.

The above procedure was then repeated for coarser fractions at a different settling time. The fractions produced in this way are shown in figures 3 and 4. As can be seen from these photomicrographs, the size grading of the powder is fairly good. Average sizes are 1.5 and 7 microns in the size ranges 0 to 3 and 3 to 10 microns, respectively. If more sedimentations had been made of each size fraction, a clearer, sharper separation might have resulted.

The number of sedimentations necessary to give a required degree of separation can be easily calculated. If 30 percent of the material of a given size is removed each time, then 70 percent will remain. The next sedimentation will remove 30 percent of the remaining 70 percent, or 21 percent of the original, and so on. This will be found to require eight sedimentations to remove 94.2 percent, or six sedimentations to remove 88 percent.

(b) ELUTRIATION

Size separations were made with the Cooke elutriator.[1] The apparatus built for the present research was modeled after the original Cooke apparatus, with some slight modification to meet the

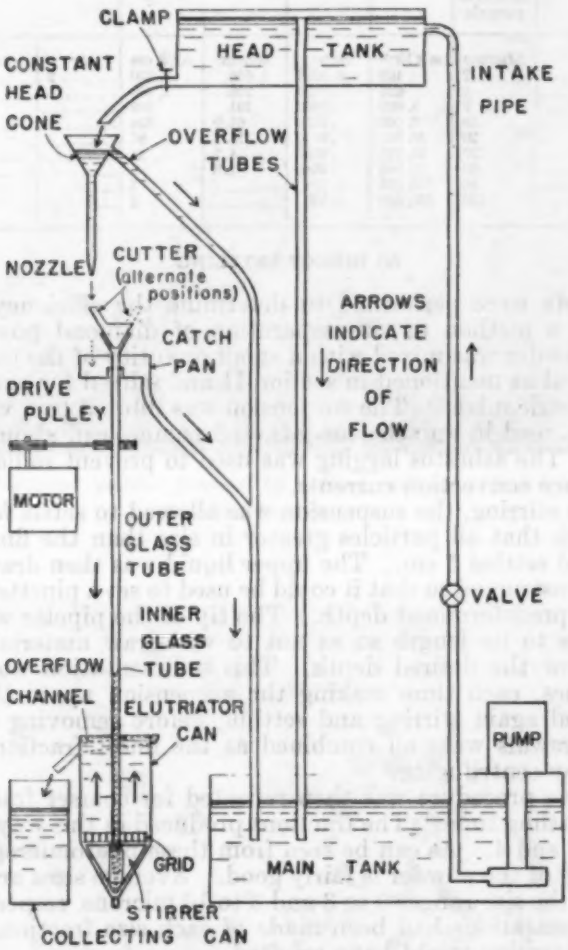

FIGURE 5.—*Diagram of Cooke elutriator.*

conditions in the constant-temperature room. A 0.1-percent-gelatin solution, made as indicated in section II, was used.

Figure 5 is a diagram of the main elements; some of the parts are shown in figure 6. The stirrer blade is shown in figures 5 and 6 at the lower end of the glass tubes. It consists of two perforated metal vanes. Above this is a metal grid, and both elements are surrounded by the elutriator can.

[1] S. R. B. Cooke, A new short column hydraulic elutriator, U. S. Bureau of Mines Report of Investigation No. 3333 (1937).

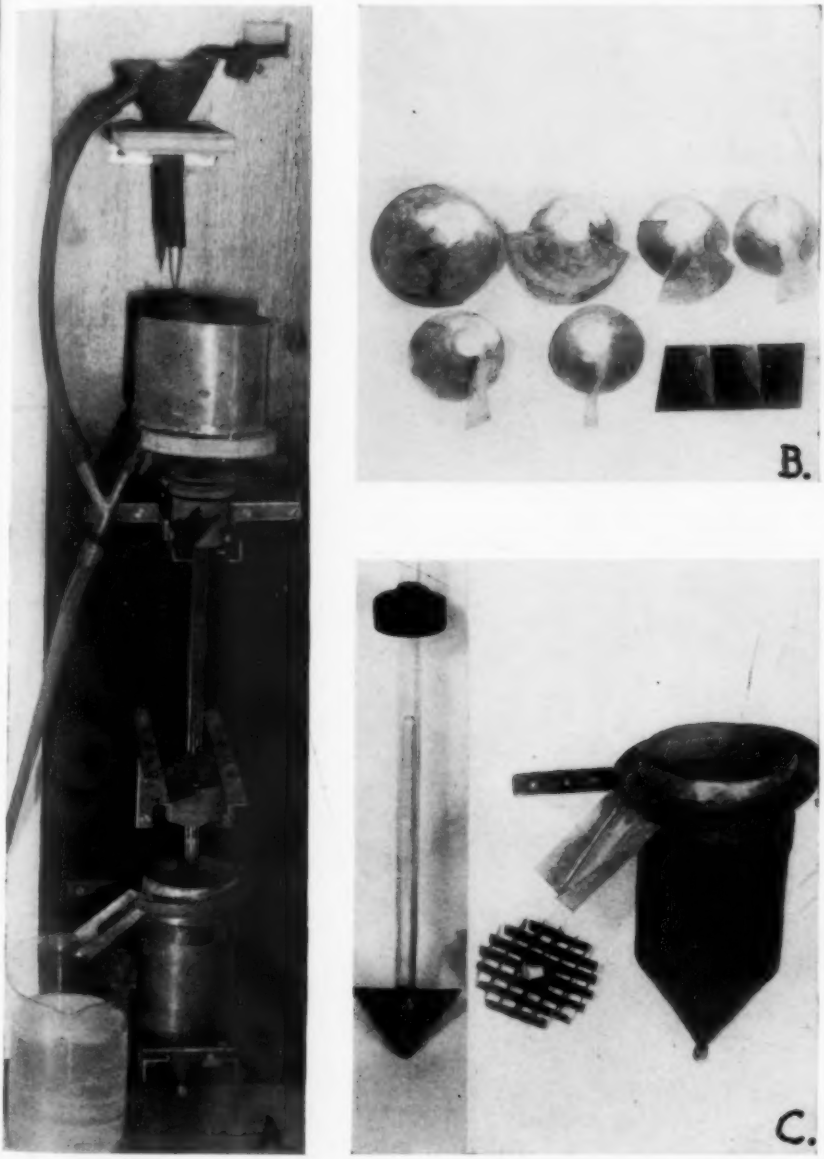

FIGURE 6.—*Cooke elutriator and parts.*

A, Assembled elutriator; *B*, the 6 cutters (360, 180, 90, 45, 22½, and 11¼ degrees) and 2 nozzles; *C* (left to right), glass tubes with stirrer, grid, and elutriator can with overflow channel.

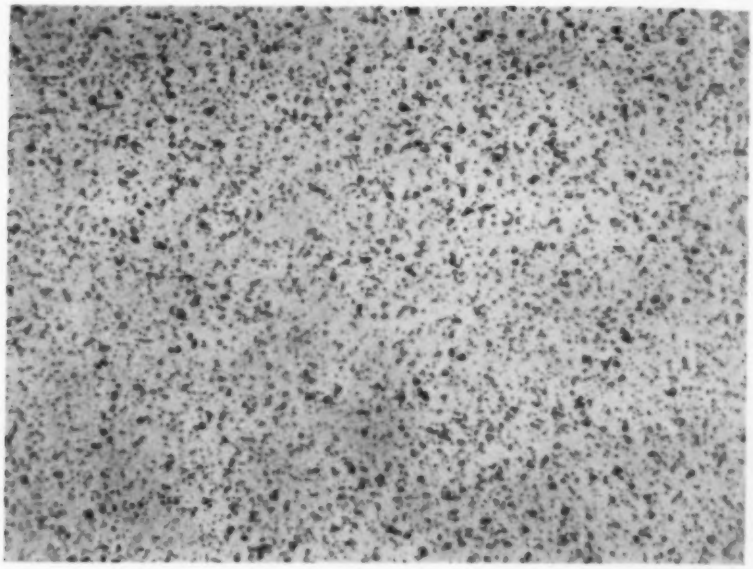

FIGURE 7.—*Elutriated diamond powder fraction, average size 1 micron.*
Magnification, × 400.

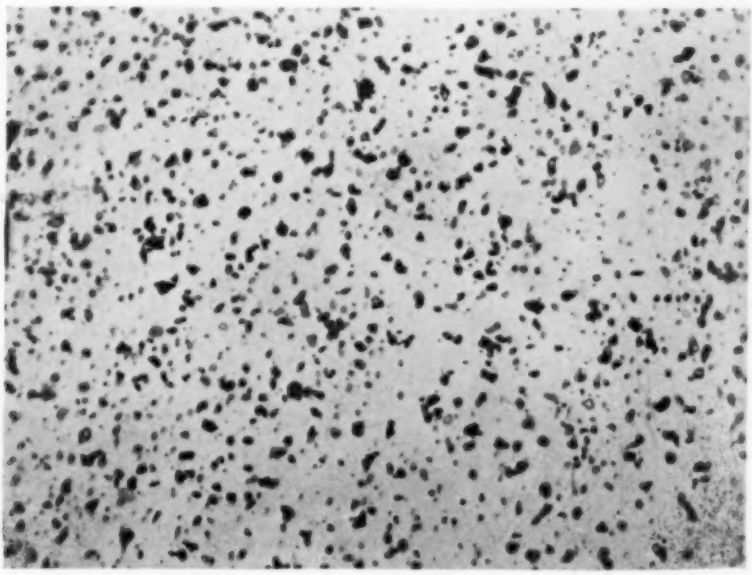

FIGURE 8.—*Elutriated diamond powder fraction, average size 2 microns.*
Magnification, × 400.

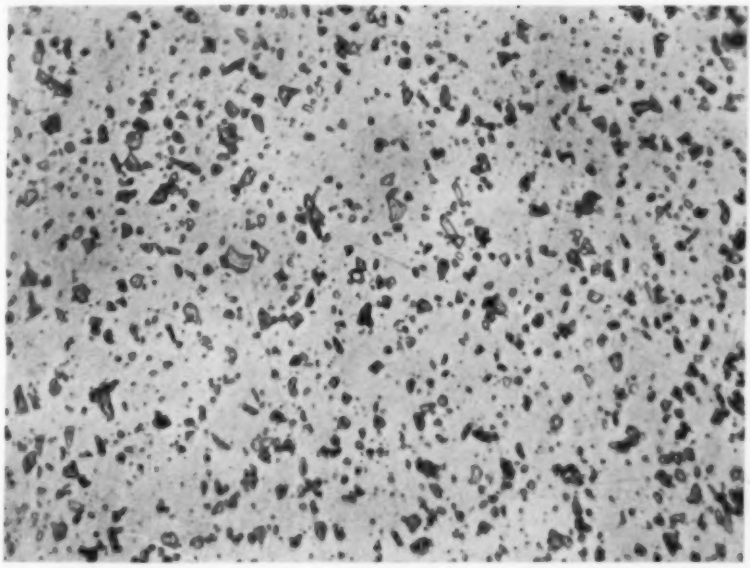

FIGURE 9.—*Elutriated diamond powder fraction, average size 5 microns.*
Magnification, × 400.

Operation of the machine is quite simple. A slurry of diamond powder and gelatin solution is introduced into the open top of the elutriator can. Gelatin solution flows down an outer glass tube and overflows into an inner glass tube to enter the elutriator can at its lower end, flows up and over the lip of the can into the overflow channel, then into a collecting can. Arrows in the diagram indicate the direction of flow. The rate of upward flow of liquid determines the grain size washed over the lip of the can.

In order to obtain a definite rate of flow, a constant head cone, cutter, and nozzle are necessary. The constant head cone provides the nozzle with a stream of liquid under constant pressure. The nozzle is so made as to deliver a definite volume of liquid per minute. As the fine sizes require flow rates of very small magnitude, a system of cutters is employed. These cutters are sectors of cones made of metal or celluloid. When the glass tube revolves at a constant rate (about 25 rpm), the cutter takes a definite portion of the stream from the nozzle, the remainder flowing back into the main tank. Cutters are of various sizes, 360 degrees for all the flow, 180 degrees for half the flow, etc.

By careful choice of nozzle and cutter any upward rate of flow may be obtained. For example, if the upward rate of flow just exceeds the sedimentation velocity for a 1-micron particle of diamond, then all particles 1 micron or smaller will overflow and be recovered in the collecting can. This overflow process is continued until examination of the overflow shows that no more particles 1 micron or smaller remain in the elutriator. The cutter can then be changed for a larger one to produce a greater flow such that the next desired size fraction is removed.

The stirrer is used to agitate the diamond slurry and prevent aggregation. In order to prevent turbulent effects caused by the rotation of the stirrer blade, a grid is used. This grid prevents any rotary motion of liquid in the upper part of the can and forces the liquid to rise vertically.

The diamond powder is then removed from the gelatin solution by the following method. For coarser sizes of powder (down to 15 to 20 microns) large volumes of liquid are encountered, and the separation takes place in two steps. First, the suspension is allowed to stand for a day, which brings the powder down to the bottom of a container about 10 inches deep. The excess liquid is decanted. Second, the slurry at the bottom is evaporated or centrifuged to remove the remaining water. After this, the powder is cleaned with hydrofluoric, nitric, and sulfuric acids in a platinum dish.

For the finer fractions, the volume of liquid from the elutriator is seldom more than a few liters. In this case, the liquid is separated by centrifuging and decantation of the supernatant liquid. The powder is collected, the excess liquid is evaporated, and the powder subjected to the cleaning process.

For a larger installation on a commercial scale it might be desirable to use a basket type or a continuous centrifuge. The cleaning in that case could be done with hot hydrochloric acid and hot dichromate-sulfuric acid cleaning solutions, followed by rinsing, filtration, and final ignition.

As diamond powder is relatively expensive, preliminary test runs in the elutriator were made with fluorite, which is quite similar to diamond in some of its physical properties. Both are cubic, with good octahedral cleavage, have similar densities (3.25 and 3.5), and have the same electric charge in water.

With fluorite, fractions were produced with uniform grain size. Four fractions were made, 0 to 2.5, 2.5 to 5, 5 to 7.5, and 7.5 to 10 microns. The average sizes, determined microscopically, of the fractions were 2, 5, 7, and 9 microns.

A charge of diamond powder was next used. Six fractions and a residue in the elutriator were recovered. Three of these fractions are shown in figures 7, 8, and 9. The size ranges (in microns) are 0 to 2, 1 to 3, and 2 to 7. Average sizes for these grades are 1, 2, and 5 microns.

There are several reasons to account for the better uniformity of the size grading of fluorite as compared to the diamond powders. The fluorite fractions were made continuously, whereas when running the diamond powder several shutdowns of the machine were necessary. The lack of reservoir capacity for the gelatin solution prevented overnight operation and, therefore, the machine was shut down at night. However, in a commercial installation enough fluid capacity could be made available so as to avoid the necessity of fairly constant attendance in order to maintain the supply of elutriator fluid. As a result of these shutdowns there was some flocculation of the diamond powder. Also it is believed that the diamond powder requires longer and more intense stirring to break up aggregations.

IV. DISCUSSION

Other methods that might be used for the size grading of diamond powders include the British centrifuge method and air elutriation.

The first of these methods is described in a British report.[2] No work was done at the Bureau in sizing powder by this method, but the powders so produced have been examined and found to be quite uniform in size. Between 1939 and 1941 they were the best to be had in this country. For large-scale production the method is believed to have certain disadvantages—the time required for centrifuging under constant attention of an operator tends to make the process uneconomical. There is often difficulty in controling the time of centrifuging, especially for larger sizes. The equipment and supplies are relatively expensive. On the other hand, this is a simple process that does good grading.

The air elutriator offers no distinct advantages over the liquid apparatus, except that the finished product requires no cleaning. However, air elutriation equipment is commercially available and has been used on diamond powder and other products.[3,4] It was not tried

[2] Report 7821, Research Laboratories of the General Electric Co., Ltd. (1941).
[3] P. S. Roller and P. V. Roundy, Jr., Surface area of portland Cement—Symposium on new methods for particle size determination in the subsieve range. Am. Soc. Testing Materials (1941).
[4] P. S. Roller, Measurement of particle size with an acurate air analyser, Proc. Am. Soc. Testing Materials **32**, pt. II, 607 (1932).

in this investigation because the equipment was not available at the time.

This work has indicated that the Cooke elutriator is very well suited for the size grading of diamond powder. It requires little attention as compared to other methods.

Probably the most economical way to operate the Cooke machine commercially would be in the form of a battery of five or more in parallel. If the tanks were sufficiently large, it is evident that one head tank and one main tank and pump could serve several elutriators. Also one motor and one speed reducer could drive the stirrers and cutters of several machines. One large tank could receive the overflow from several machines.

The attention required by a battery of elutriators would be little more than that for a single one. It was found that about 15 minutes would be required to change cutters and receptacles for each fraction for a battery of five elutriators. Loading would take about 5 minutes to a machine, and cleaning out each machine after the last fraction has been made would take about 5 minutes.

V. COMMERCIAL STANDARD AND SPECIFICATION

As a result of a part of this work, a Commercial Standard [5] was devised by the Bureau's Division of Trade Standards. By conference with producers and consumers, this was adjusted to meet the requirements of the trade and was finally adopted on March 6, 1945. The sizes and grades as given in that standard are shown in table 5.

TABLE 5.—*Grade designation, grain size, and sieve numbers*

Grade designation [1]	Grain size (microns)		U. S. Standard Sieve number (through) [2]
	Minimum	Maximum	
1	0	2	----------
2	1	3	----------
3	1	5	----------
3X	0	6	----------
6	4	8	----------
8	6	10	----------
8X	4	12	----------
14	8	20	----------
25	13	37	----------
40	20	60	325
60	35	85	230
90	60	120	170
120	80	160	120
150	100	200	100
180	120	240	80
250	160	350	60
400	250	550	40

[1] Grades 1, 6, and 8 are narrow-range grades for exacting work in cutting and polishing fine diamond dies, sapphire bearings, etc. Grades 3X and 8X are wide-range grades desired for some purposes.

[2] United States Standard Sieve series. Sieve numbers are included for reference only. It does not necessarily follow that powders passing the sieve indicated for a grade will meet the grain-size requirements of that grade, nor that powders retained on the sieve necessarily fail to meet the grain-size requirements.

[5] Commercial Standard CS123-45, Grading of diamond powder (1945).

VI. SUMMARY

Dilute gelatin solution was the best liquid of the 30 tried for dispersing and sedimenting diamond powder.

Sieving was found to give a clean separation of the larger size fractions if the coarse fraction was washed in acetone after the sieving.

Direct settling gave size separation that was fairly good.

The Cooke elutriator was found to be the most economical of the methods tried for the size grading of diamond powder.

This work was instigated and financed by the War Production Board and the War Metallurgy Committee of the National Academy of Sciences. The study was first published as War Production Board Serial No. W–156.

WASHINGTON, January 31, 1946.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1717

Part of Journal of Research of the National Bureau of Standards, Volume 36, May 1946

PRECISION OF TELESCOPE POINTING FOR OUTDOOR TARGETS

By Francis E. Washer and Helen Brubaker Williams

ABSTRACT

The probable error of a single pointing (PE_s) is measured for a single telescope with a variety of targets. This investigation shows that, although some change in PE_s with distance does occur, the distribution of PE_s as a function of distance can usually be neglected and a value of 0.62 second assigned as a practical average. The values of PE_s for an indoor target usually show a small variation from one experienced observer to another, and from right to left eye of the same observer. There is also a measurable systematic difference in pointing between the right eye and the left eye of the same observer. In outdoor pointing, a long-period error or drift is usually superposed upon the short-period errors.

CONTENTS

	Page
I. Introduction	479
II. Apparatus and method of measurement	480
III. Results of measurement	480
1. Indoor target	480
2. Outdoor targets	481
3. Effect of distance	481
4. Consistency	482
5. Observer differences with an indoor target	484
(a) Probable error of a single pointing	484
(b) Pointing differences	486

I. INTRODUCTION

When pointings are made with a telescope, the probable error of a single setting is of interest. In this paper the error, associated with the optical characteristics of the problem, is discussed. The errors present may be either accidental or systematic. The study of the accidental errors is emphasized herein. These accidental errors arise partly from the conditions prevailing along the optical path and partly from limitations on the part of the observer. The former are greater in magnitude. In outdoor pointing, the image of the target formed by the objective and seen through the ocular is constantly oscillating with respect to the cross hairs mounted in the focal plane of the objective. Setting the cross hairs into apparent coincidence with the image of the target formed by the objective and seen through the ocular is, for the most part, a matter of deciding upon the mean position of the image of the target and setting the cross hairs thereon.

Even when the image of the target appears stationary, an error of pointing still persists and is measurable.

In the present work, the pointing errors for a given telescope have been measured for a number of outdoor targets and an average value determined for the probable error of a single pointing. The figure so determined is of interest in that it is the limit of precision that can be attained in outdoor pointing under average daylight conditions and over a terrain that consists partly of park area and partly of city residential and business sections. When, therefore, measurements are being made, under similar conditions, that involve pointing accuracy, it is profitless to attempt, by further refinement of the equipment, to better the precision if this limit has already been reached. For outdoor pointing, the average value of the probable error of a single setting found here is 0.62 second.

It is the purpose of this paper to present a concise account of the experimental results. A more detailed account, including a bibliography and summary of previous work, is being published elsewhere.[1]

II. APPARATUS AND METHOD OF MEASUREMENT

The apparatus consists of a telescope from a surveying level with an effective aperture of 39 millimeters and a magnification of 3 diameters, and a means of varying the pointing without disturbing the telescope. This is accomplished by a weak prism, placed in front of the telescope objective, capable of rotation about its axis. As the deviation of a parallel beam of light caused by a prism is a function of the angle of incidence, the image of the target can be made to move with respect to the telescope cross hairs by rotating the prism.

Observations are made in groups of 10 and the probable error of a single pointing is determined from these data. Five 10-groups are usually taken in succession to constitute a single run. The total error of calibration is kept under 2 percent, and the least reading in seconds of the instrument is less than one-fifth the magnitude of the least probable error of a single pointing. The probable error of a single pointing, PE_s, measured in seconds, is computed from the approximate formula

$$PE_s = \frac{0.8453k}{\sqrt{n(n-1)}} \sum r \qquad (1)$$

where n is the number of observations, $\sum r$ is the sum of the residuals and k is the calibration constant of the prism.

III. RESULTS OF MEASUREMENT

1. INDOOR TARGET

Although the main purpose of the present work is the determination of PE_s for outdoor targets, the PE_s for the given telescope was first measured with an indoor target. Thus when, as is later found, the PE_s for an outdoor target is greater than the value obtained with an indoor target, one can be sure that the limit on PE_s is being placed by the conditions of outdoor pointing and not by limitations of the

[1] F. E. Washer and H. B. Williams, J. Opt. Soc. Am. 36 (June, 1946).

telescope itself. Accordingly, the experiment was first performed indoors with a vertical wire mounted in the focal plane of a collimator as target.

It is found that, for the conditions under which these measurements are made, the accuracy of pointing is not affected by aperture or color of light and that the value, PE_s=0.25 second, is the optimum value that can be expected for indoor pointing with this instrument.

2. OUTDOOR TARGETS

The outdoor test objects consist of a number of distant targets that are readily discernible from the laboratory. Several series of observations were made on each target. In most cases, measurements were made independently by two observers identified as W and B. The results of measurement are assembled in table 1.

TABLE 1.—*Probable error of a single pointing for each of two observers with distant targets*

Target	Range	Observer W		Observer B		Average	
		PE_s	N	PE_s	N	PE_s	N
	m	sec		sec		sec	
Collimator	2	0.25	600			0.25	600
Radio	100			0.45	50	.45	50
Tilden	323	.46	100	.42	150	.44	250
Sedgwick	445	.36	200	.50	200	.43	400
Broadmoor	708			.57	300	.57	300
Orfway	905	.61	300	.44	100	.57	400
Klingle	1,153	.60	200	.57	100	.59	300
Swank	1,300	.58	300	.58	200	.58	500
Majestic	2,722	.51	150	.52	100	.51	250
Baptist	3,000			.73	200	.73	300
Unity	3,080	.75	600	.67	200	.73	800
Howard	4,505	.90	50	.72	50	.81	100
Clock	4,779	.66	500	.71	150	.67	650
Trinity	5,553	.65	200			.65	200
Capitol	7,554	.92	100	.69	100	.80	200
Bradbury	13,624	.86	50	.97	50	.92	100
Average		0.64	2,750	0.60	1,950	0.62	4,700

It is evident from table 1 that the values of PE_s for a given target do not differ greatly from one observer to the other when n is large. Furthermore, assuming that any effect of distance can be neglected, the grand average of 2,750 observations by W differs by only 0.04 second from the grand average of 1,950 observations by B. The differences between the PE_s values for the two observers on a given target when n is small are no greater than those that sometimes occur between successive groups for a single observer. The average PE_s for 4,700 observations by two observers is 0.62 second.

3. EFFECT OF DISTANCE

In the preceding section it has been assumed that PE_s is independent of the distance separating observer and target and a value assigned to it on that basis. This procedure is justified practically because of the seemingly random scattering of the PE_s values with

respect to distance. Also, so many variables enter into pointing accuracy that the effect of distance is screened by the greater influence of other factors that are not subject to control, such as state of the weather and conditions of visibility.

Notwithstanding these handicaps, least squares solutions were made on the basis of several assumptions. The solution that appeared most satisfactory is

$$PE_s = 0.064d^{\frac{1}{2}} + 0.19, \tag{2}$$

where d is the distance separating target and observer. In figure 1, the values of PE_s predicted by equation 2 are plotted as a function of distance. The observed values of PE_s are shown as circles. It is

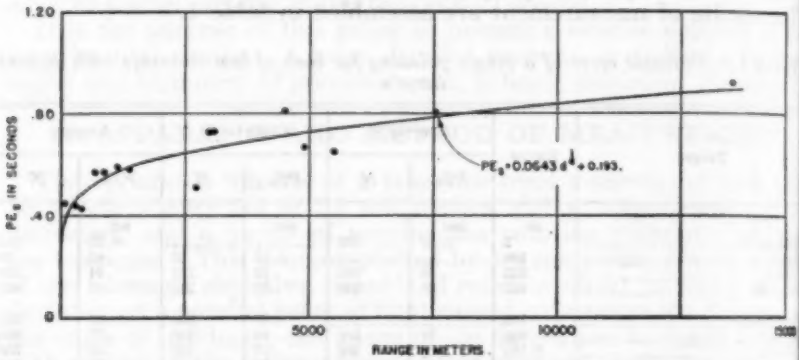

FIGURE 1.—*Probable error in a single pointing* (PE_s) *versus distance.*

The points indicate observed values. The solid curve is the relation computed from the formula $PE_s = 0.064d^{\frac{1}{2}} + 0.19$.

evident that on the whole there is fairly good agreement. In contemplating the points of disagreement, it may be mentioned that there may not have been enough variation in the viewing conditions to bring about a truly average value for each target.

4. CONSISTENCY

It was early noted that, when a set of 50 observations, comprising five 10-groups, is made, the mean values of deviations in the line of sight for the various 10-groups in a 50-set are not consistent. In other words, the means of the 10-groups appeared to drift or oscillate as if a long slow period of change was superposed on the short-period changes that occur in a 10-group. For example, such a change would be introduced by variation in a horizontal air-temperature gradient perpendicular to the line of sight. To test for the existence of such a long-period error, each of the five 10-group means in a 50-set is treated as a single observation, and the probable error, C, of such a single mean is computed from the formula

$$C = \frac{0.8453}{\sqrt{n(n-1)}} \Sigma r. \tag{3}$$

If the distribution of the observations contained in the 50-set is normal then the value of C should be approximately equal to the average probable error of the mean, $\overline{PE}_m$, for the five 10-groups, which is obtained from the formula

$$\overline{PE}_m = \frac{\overline{PE}_s}{\sqrt{10}} \tag{4}$$

The values of $\overline{PE}_m$ and $\overline{C}$ for some of the targets are given in table 2, where, however, these data are averaged for a number of 50-sets. Values are also listed of the difference $\overline{C}-\overline{PE}_m$ to facilitate comparison. If no long-period error is present, the values of $\overline{C}-\overline{PE}_m$ ought to be relatively small, and the average over all the targets ought to be approximately zero. However, the table shows that $\overline{C}$ is greater than $\overline{PE}_m$ in all cases for observer B and in 10 out of 12 cases for observer W. Therefore, it may be stated that a long-period error does exist. For observer W, the average value of $\overline{C}-\overline{PE}_m$ is 0.08 second, and for observer B, the value is 0.36 second.

TABLE 2.—*Consistency of observations for each of two observers with distant targets*

Target	Range	Observer W				Observer B			
		$\overline{PE}_s$	$\overline{PE}_m$	$\overline{C}$	$\overline{C}-\overline{PE}_m$	$\overline{PE}_s$	$\overline{PE}_m$	$\overline{C}$	$\overline{C}-\overline{PE}_m$
	m	sec	sec	sec	sec	sec	sec	sec	sec
Radio	100					0.45	0.14	0.86	0.72
Tilden	323	0.49	0.15	0.14	−0.01	.42	.13	.62	.49
Sedgwick	445	.36	.11	.16	.05	.50	.16	.63	.47
Broadmoor	703					.57	.18	.70	.52
Ordway	905	.62	.20	.29	.09	.44	.14	.50	.36
Klingle	1,153	.62	.20	.30	.10	.57	.18	.42	.24
Frank	1,399	.55	.17	.31	.14	.58	.18	.42	.24
Majestic	2,722	.51	.16	.16	.00	.52	.16	.21	.05
Baptist	3,000					.73	.23	.59	.36
Unity	3,080	.75	.24	.34	.10	.67	.21	.63	.42
Howard	4,504	.90	.28	.30	.02	.72	.23	.45	.22
Flock	4,779	.67	.21	.42	.21	.71	.22	.53	.31
Trinity	5,533	.65	.21	.40	.19				
Capitol	7,554	.92	.29	.31	.02	.69	.22	.54	.32
Bradbury	13,624	.86	.27	.37	.10				
Average		0.66	0.21	0.29	0.08	0.58	0.18	0.55	0.36

The quantity $\overline{C}-\overline{PE}_m$ is very much greater for observer B than for observer W, and as the values of PE_s are closely comparable for both, this indicates the presence of yet another error in addition to drift. In seeking an explanation for this large difference between observers W and B, it was recalled that observer B used the left and right eyes for alternate 10-groups in a 50-set, whereas observer W used the right eye only. At the time this practice was initiated it was believed that no difference should arise therefrom. However, on analyzing the averages of the means for right and left eyes, a systematic difference in the direction of pointing for right and left eyes appears to be definitely present for observer B. This difference, which is designated

OD—OS, although showing some difference from one 50-set to another, is generally positive. It may be mentioned that systematic differences between the settings made by the right and left eye are evident in tables of data shown in a paper by Labitzke,[2] which deals with bisection errors. On the basis of Labitzke's work, it appears that the average of settings made by either eye is likely to show a systematic error but that the magnitude is not the same for each eye, thus an *OD—OS* value exists for each individual, although it is improbable that the value will be the same for all individuals.

5. OBSERVER DIFFERENCES WITH AN INDOOR TARGET

Having noted the pointing differences for the right and the left eye with outdoor targets in the case of observer B, it seemed worth while to investigate this matter further by using the indoor target to eliminate the uncertainty arising from the long air column present with the outdoor target. A series of observations was made by each of six observers [3] at various apertures of the viewing telescope, ranging from the full aperture of 39 millimeters to an aperture of 6.8 millimeters. Whereas the outdoor observations by observer B usually had three 10-groups of left-eye pointing to two 10-groups of right-eye pointing, the indoor work involved an equal number of 10-groups for each eye. Accordingly, each observer made at least 60 observations in groups of 10, alternating the use of the right and the left eye.

(a) PROBABLE ERROR OF A SINGLE POINTING

The values of PE_s for the six observers are shown in figure 2. PE_{OD} and PE_{OS} are the probable errors of single pointings with right and left eyes, respectively, and PE_s is the average for the two eyes. It may be noted in figure 2 that there is usually a difference between the two eyes in the magnitude of the probable error of a single pointing. Whether this difference is sufficiently great to be significant in most cases is problematical, as the average departure of PE_{OD} or PE_{OS} from PE_s for all observations shown is 8.5 percent. However, it seems reasonable that each eye should be considered as a separate individual, and, on this assumption, perhaps some significance may be attached to this difference. In any event, it is interesting to note that the lowest PE_s is not always obtained with the eye most generally used for observing by each individual. For example, although observers C and W, who normally observe with their left and right eye, respectively, do have lower probable errors for those eyes, observer B, who generally observes with the left eye, and observers T, E, and F, who normally use the right eye, all have a little greater error at most apertures when observing with the eye normally used.

It should be pointed out that observers E and F, whose probable errors range much higher than those of other observers and whose differences in probable error for the right and the left eye are more pronounced, were at this time very inexperienced. Observers W, T, B, and C, the most experienced, have generally the lowest and least erratic probable errors. These patterns, then, of individual

[2] P. Labitzke, Untersuchung uber psychologisch—und physiologische Bisektionsfehler, Z. Instrumentenk. 44, 61 and 165 (1924).

[3] The four additional observers cooperating in this work were L. W. Tilton, T; F. A. Case, C; E. P. Samuels, E; and F .C. Samuels, F.

differences in observation are good evidence that experience is conducive to precision in pointing.

In the upper graph of figure 3, the probable errors of a single observation of pointing made with right and left eyes are averaged for

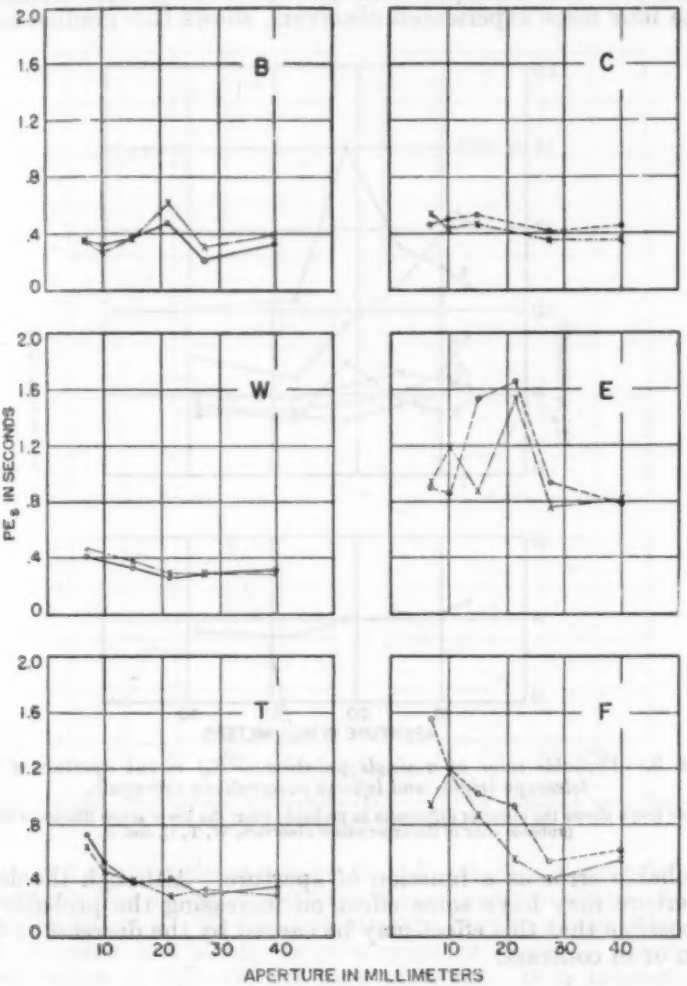

FIGURE 2.—*Probable error of a single pointing (PE_s) versus aperture of the viewing telescope.*

Values of PE_s for right-eye pointing are marked ○ and those for left eye pointing are marked X.

each individual. Here may be seen more strikingly the difference in the magnitude of the probable error between the more experienced and the inexperienced observers. For each observer the probable error tends to decrease slightly when the aperture is decreased from 39 to 27.5 millimeters. Then the probable error begins to increase gradually as the aperture is decreased progressively from 27.5 to 6.8

millimeters. This decrease in probable error followed by an increase when the aperture is stopped down progressively was also found by Tilton [4] in his investigation of pointing accuracy in connection with prism size in minimum deviation refractometry. The lower graph of figure 3, in which the probable errors at each aperture are averaged for the four more experienced observers, shows this gradual increase

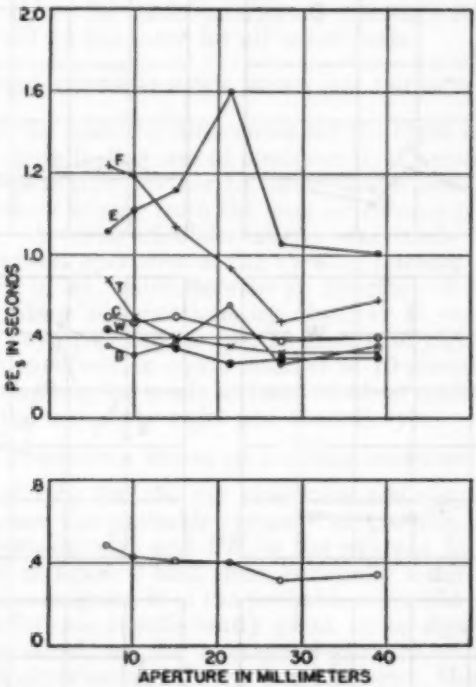

FIGURE 3.—*Probable error of a single pointing (PE_s) versus aperture of viewing telescope (right- and left-eye observations averaged).*

The upper graph shows the observer differences in probable error; the lower graph illustrates the average probable error of the experienced observers, W, T, C, and B.

in probable error as a function of aperture. Although the decrease in aperture may have some effect on increasing the probable error it is possible that this effect may be caused by the decrease in illumination or in contrast.

(b) POINTING DIFFERENCES

Successive 10-groups of observations were made with right and left eyes alternately, and it was found that the mean of the 10-group settings for the right eye differed from the mean of the 10-group settings for the left eye; that is, the observers tended to point more to one side of the target with one eye than with the other. These eye differences

[4] L. W. Tilton, Prism size and orientation in minimum deviation refractometry, BS J. Research 6, (1931) RP262.

are tabulated under the column *OD—OS* in table 3 for each observer. M_D and M_S are the probable errors of the mean for right and left eye, respectively. R is the probable error of the difference in the means for right and left eyes. It may be seen in table 3 that in 28 out of 34 instances, the values of *OD—OS* are greater than R; moreover, the value of *OD—OS* ranges from 1 to 17 times as great as R, and in 12

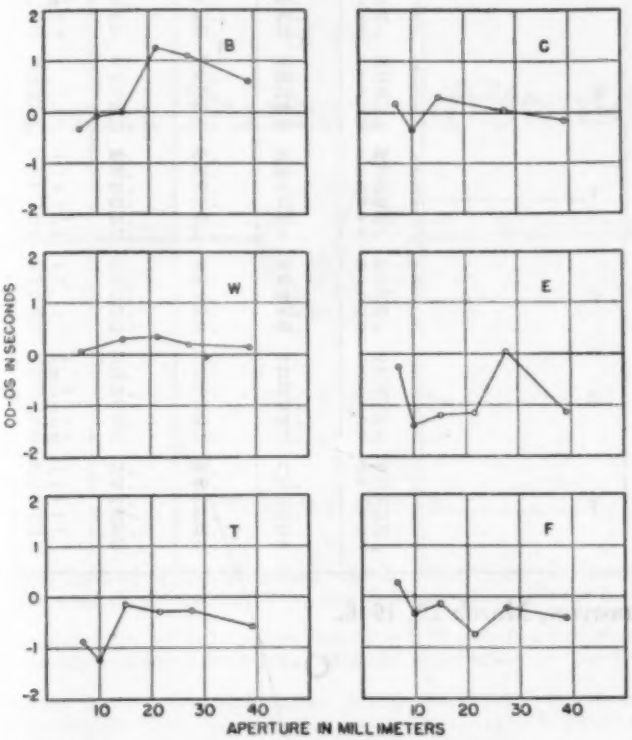

FIGURE 4.—*Right- and left-eye differences (OD—OS) in pointing as a function of aperture for individual observers.*

instances is 4 or more times greater than R, which indicates definitely that there is a real difference between the settings made with the right eye and the left eye. There is no attempt here to explain the cause of this difference but merely to give evidence thereof. Figure 4 illustrates values of *OD—OS* for each observer. It is interesting to note that observer T has all negative values for the differences and observers E and F have predominately negative, whereas observer W has all positive values, and observers B and C have a majority of positive values.

TABLE 3.—*Individual eye differences in pointing and their probable errors*

Observer	Aperture	M_D	M_S	R	$OD-OS$
	mm	sec	sec	sec	sec
B	39.0	±0.03	±0.04	±0.05	0.61
	27.5	.04	.06	.07	1.09
	21.4	.09	.12	.14	1.26
	15.0	.05	.05	.07	−0.01
	10.0	.04	.04	.06	−.08
	6.8	.04	.05	.07	−.34
W	39.0	.04	.04	.05	.15
	27.5	.05	.05	.08	.22
	21.4	.05	.05	.07	.41
	15.0	.06	.07	.09	.28
	6.8	.08	.09	.12	.06
T	39.0	.06	.05	.09	−.57
	27.5	.06	.06	.09	−.26
	21.4	.08	.06	.10	−.29
	15.0	.07	.08	.10	−.14
	10.0	.10	.09	.13	−1.23
	6.8	.13	.12	.18	−0.88
C	39.0	.08	.06	.10	−.16
	27.5	.08	.06	.10	.03
	15.0	.10	.09	.13	.30
	10.0	.09	.08	.12	−.35
	6.8	.06	.10	.13	.17
E	39.0	.10	.11	.15	−1.13
	27.5	.17	.14	.22	0.05
	21.4	.31	.28	.42	−1.15
	15.0	.28	.17	.32	−1.20
	10.0	.16	.22	.27	−1.40
	6.8	.17	.17	.24	−0.25
F	39.0	.11	.10	.15	−.43
	27.5	.10	.08	.13	−.23
	21.4	.17	.10	.20	−.77
	15.0	.18	.16	.24	−.16
	10.0	.22	.21	.31	−.35
	6.8	.28	.17	.33	.25

WASHINGTON, March 29, 1946.

○